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APPLICATION DE LA RÉACTION DE MEERWEIN À LA BENZALACÉTONE¹

PAR PHILIBERT L'ÉCUYER ET CHARLES-A. OLIVIER²

Sommaire

La réaction de Meerwein entre divers sels de diazonium aromatiques substitués et la benzalacétone a donné naissance aux dérivés de l' α -acétylstilbène suivants: l' α -acétyl-4-bromostilbène, l' α -acétyl-4-chlorostilbène, l' α -acétyl-3-nitrostilbène et l' α -acétyl-4-nitrostilbène. D'autre part la même réaction entre la benzalacétone et d'autres sels de diazonium aromatiques substitués a conduit aux dérivés du dibenzyle suivants: l' α -acétyl- β -chloro-2-chlorodibenzyle, l' α -acétyl- β -chloro-3-chlorodibenzyle, l' α -acétyl- β -chloro-2-méthylidibenzyle, l' α -acétyl- β -chloro-3-méthylidibenzyle, l' α -acétyl- β -chloro-2-nitrodibenzyle et l' α -acétyl- β -chloro-4-phényldibenzyle. Le sel de diazonium de la *p*-nitraniline et l'acide 2-furfurylacrylique ont donné naissance à l' α -(4-nitrophényl)- β -(2-furfuryl)-éthène. L'action du même sel de diazonium sur le *p*-nitrocinnamitrile a fourni l' α -cyano-4,4'-dinitrostilbène. Enfin l'hydrolyse de l' α -chloro-4-chlorohydrocinnamitrile a donné l'acide α -chloro-4-chlorohydrocinnamique et finalement l'acide 4-chlorocinnamique par l'élimination de HCl.

Introduction

Meerwein et ses collaborateurs (12) ont montré que l'action des chlorures de diazonium aromatiques sur les composés carbonyles possédant une double liaison entre les carbones α et β conduit à la synthèse de dérivés du stilbène. Avec les aldéhydes, les nitriles et les acides aromatiques α , β -non saturés le groupement phényle, qui est introduit par l'intermédiaire du sel de diazonium, se fixe sur le carbone α de la double liaison oléfinique (1, 2, 3, 4, 5, 10, 12) et les produits de la réaction sont des dérivés non-saturés du stilbène. Par contre, lorsque la condensation se fait avec les esters aromatiques, HCl s'additionne à la double liaison au cours de la réaction et les composés obtenus sont saturés. Dans les mêmes conditions, les chlorures de diazonium aromatiques réagissent également avec l'acrylate de méthyle et l'acrylonitrile (9). Dans ce dernier cas cependant le groupement phényle se fixe sur l'atome de carbone β du composé non-saturé au lieu de se joindre à l'atome de carbone α , pendant que HCl s'additionne sur la même liaison éthylénique.

Dans une étude précédente (11) il a été constaté que la réaction de Meerwein peut s'effectuer entre des amines aromatiques substituées et des acides aromatiques non-saturés également substitués. Cette condensation fournit une

¹ Manuscrit reçu le 25 mars 1949.

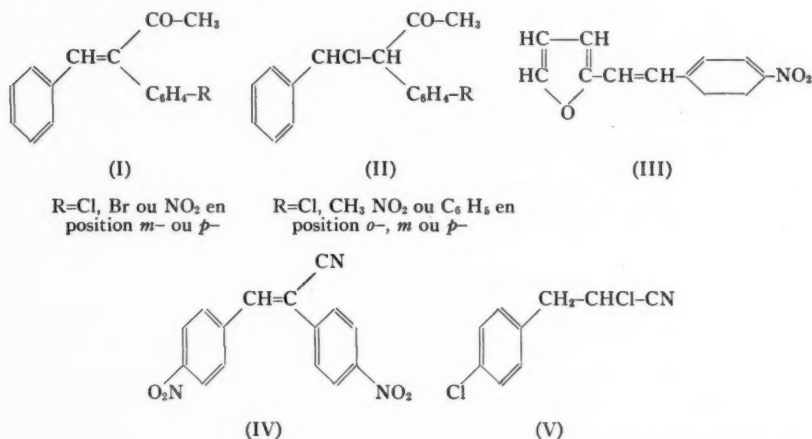
Contribution du Département de chimie de l'Université Laval, Québec (Qué.).

² Boursier du Conseil National des Recherches.

méthode satisfaisante pour la préparation des dérivés du stilbène avec des groupements substituants dans n'importe quelle position des deux anneaux du benzène.

En raison de l'intérêt qu'offre certains composés du stilbène possédant des substituants dans la partie aliphatique de la molécule en même temps que dans les anneaux benzéniques, nous avons cru bon d'étudier la possibilité d'appliquer la réaction de Meerwein à la benzalacétone et à ses dérivés.

La condensation entre la benzalacétone et les sels de diazonium de quatre amines aromatiques: la *p*-bromaniline, la *p*-chloraniline, la *m*- et la *p*-nitranilines, se passe normalement. Le groupement phényle se fixe sur l'atome de carbone non-saturé α pour donner les quatre dérivés α -acétylés du stilbène: α -acétyl-4-bromostilbène, α -acétyl-4-chlorostilbène, α -acétyl-3-nitrostilbène et α -acétyl-4-nitrostilbène (I).



Toutefois avec d'autres amines aromatiques substituées l'*o*- et la *m*-chloraniline, l'*o*- et la *m*-toluidine, l'*o*-nitraniline et le *p*-aminodiphényle les composés qui ont été isolés étaient les dérivés du dibenzyle suivants: α -acétyl- β -chloro-2-chlorodibenzyle, α -acétyl- β -chloro-3-chlorodibenzyle, α -acétyl- β -chloro-2-méthyldibenzyle, α -acétyl- β -chloro-3-méthyldibenzyle, α -acétyl- β -chloro-2-nitrodibenzyle et α -acétyl- β -chloro-4-phényldibenzyle (II), HCl s'étant additionné à la double liaison. Il est difficile d'expliquer pourquoi HCl s'additionne à la double liaison, dans certains cas, tandis qu'il ne le fait pas dans d'autres. Nous avons pu constater cependant que dans les composés chlorés HCl n'est pas solidement fixé à la molécule et qu'il se dégage lorsque la substance est chauffée au-dessus de son point de fusion à la pression atmosphérique.

Nous avons tenté la condensation de la *m*-nitrobenzalacétone et de la *p*-nitraniline. La réaction semble se passer normalement, mais il fut impossible de purifier le produit obtenu. Par cristallisation, de beaux cristaux

se formaient alors que la solution était encore chaude, mais au cours du refroidissement une substance goudronneuse se déposait inévitablement sur eux et les faisait se ramollir. Il semble donc qu'il y a trop peu de différence entre les propriétés physiques des substances en présence pour permettre une purification convenable. Après une réaction de Meerwein on retrouve toujours inchangée une certaine quantité du composé carbonyle non-saturé. Comme le point d'ébullition de la benzalacétone substituée est trop près de celui du composé synthétisé, il est impossible d'éliminer la première par la distillation dans le vide. Il semble aussi que la solubilité des deux substances dans les solvants organiques ordinaires soit trop voisine pour en permettre la purification par la cristallisation. Pour ces raisons il nous a paru inutile de tenter la condensation de Meerwein entre d'autres benzalacétones substituées et les sels de diazonium aromatiques.

Incidentement, comme nous disposons d'une certaine quantité d'acide furfurylacrylique, nous avons tenté sa réaction avec la *p*-nitraniline et l' α -(4-nitrophényl)- β -(2-furfuryl)-éthylène (III) a été isolé de la façon habituelle. Depuis la communication de nos résultats au Conseil National des Recherches la même préparation a été décrite par Brown et Kon (6).

Nous avons pu vérifier après Koelsch (9) que, dans l'application de la réaction de Meerwein à l'acrylonitrile, le groupement aryle entre en position β et qu'il y a en même temps addition de HCl sur la double liaison le chlore se fixant sur le carbone α . Pour obtenir les dérivés de l' α -cyanostilbène correspondants il faut donc éliminer une molécule d'acide chlorhydrique sous l'action de la pipéridine. C'est ainsi que, après une première condensation de la *p*-nitraniline avec l'acrylonitrile et l'élimination de HCl à l'aide de la pipéridine pour donner naissance au *p*-nitrocinnamonitrile nous avons obtenu par la réaction de ce dernier avec le sel de diazonium de la nitraniline, le 4,4'-dinitro- α -cyanostilbène (IV).

La réaction avec l'acrylonitrile offre aussi la possibilité de préparer des acides α -chlorocinnamiques. Il suffit d'hydrolyser en milieu chlorhydrique les α -chlorohydrocinnamonitriles (V) pour les obtenir.

Partie Expérimentale

Toutes les réactions rapportées ici ont été effectuées à partir de 0.1 mole d'amine et d'une quantité équimoléculaire du composé carbonyle. La quantité des autres substances nécessaires à la réaction demeure constante pour cette quantité de réactifs. Quant au solvant, l'acétone, il faut en mettre une quantité suffisante pour maintenir le composé carbonyle en solution.

Un mélange d'amine (0.1 mole), d'acide chlorhydrique à 25% (50 ml.) et de glace (50 g.) est diazoté à une température inférieure à 5° C. par l'addition graduelle d'une solution de nitrite de sodium (8.4 g.) dans l'eau (16 ml.). Le chlorure de diazonium ainsi formé est versé dans un mélange refroidi du composé carbonyle α , β -non saturé (0.1 mole) dissous dans l'acétone et

d'acétate de sodium anhydre (25 g.). L'addition d'une solution de chlorure cuivrique dihydraté (4.2 g.) dans l'eau (12 ml.) catalyse la réaction.

Celle-ci qui est caractérisée par un dégagement de gaz assez rapide, s'amorce à une température qui varie suivant les réactifs. Dans la plupart des cas la réaction débute à une température inférieure à 15° C., mais il est quelquefois nécessaire de plonger le mélange réactionnel dans un bain d'eau chaude pour l'amorcer. De toute façon une fois la réaction amorcée, elle est assez exothermique pour que la température se maintienne sans chauffage. Pendant tout le temps que dure la réaction (environ deux heures) le mélange est soumis à une vigoureuse agitation mécanique.

On soumet le tout à une distillation à la vapeur d'eau pour récupérer l'acétone et chasser les composés volatils formés pendant la réaction. On rend le résidu alcalin à l'ammoniaque, on décante la liqueur surnageante et on lave la gomme qui reste plusieurs fois à l'eau pour éliminer les dernières traces de cuivre. La gomme est ensuite dissoute dans le chloroforme ou l'éther, la solution est séchée sur du sulfate anhydre de sodium et le solvant est évaporé. Le résidu est enfin soumis à la distillation dans le vide (0.005 mm.). Le composé carbonyle non transformé passe d'abord (la benzalacétone à 80°–90° C.) et le produit de la réaction est ensuite recueilli à une température plus élevée et est cristallisé de l'alcool dilué de 80 à 95% suivant le cas.

Les principales particularités des diverses condensations et quelques propriétés physiques des substances synthétisées sont contenues dans le tableau I.

TABLEAU I
SUBSTANCES PRÉPARÉES

Réactifs		Produit de réaction	P.e. ° C. (0.005 mm.)	P.f. ° C.*	Rend., %	Analyse	
Composé carbonyle	Amine					Calculé	Trouvé
Benzalacétone	<i>p</i> -Nitraniline	I 4-NO ₂	—	147	39	N = 5.3	N = 5.4
"	<i>m</i> -Nitraniline	" 3-NO ₂	150–160	98	18	N = 5.3	N = 5.2
"	<i>p</i> -Chloraniline	" 4-Cl	130–135	105–106 (13)	45	Cl = 13.8	Cl = 13.9
"	<i>p</i> -Bromaniline	" 4-Br	140–150	137–139	10	Br = 26.5	Br = 26.1
"	<i>o</i> -Chloraniline	II 2-Cl	120–125	113–114	20	Cl = 24.2	Cl = 24.4
"	<i>m</i> -Chloraniline	" 3-Cl	125–130	90–91	39	Cl = 24.2	Cl = 24.2
"	<i>o</i> -Toluidine	" 2-CH ₃	105–115	108–109	15	Cl = 13.0	Cl = 13.5‡
"	<i>m</i> -Toluidine	" 3-CH ₃	115–125	70–71	20	Cl = 13.0	Cl = 13.1
"	<i>o</i> -Nitraniline	" 2-NO ₂	140–150	145–147 (déc.)	38	N = 9.2	N = 9.4
"	<i>p</i> -Phénylaniline	" 4-C ₆ H ₅	—	141–142	20	Cl = 11.7	Cl = 12.2
Ac. 2-furfurylacri- lique	<i>p</i> -Nitraniline	III —	140–145 (sub.)	129–130	23	Cl = 10.6	Cl = 10.7‡
4-NO ₂ -cinnamoni- trile	"	IV —	—	214–215†	12	N = 6.5	N = 6.7
Acrylonitrile	<i>p</i> -Chloraniline	V —	75	—	37	N = 14.2	N = 13.9
						Cl = 35.5	Cl = 35.6

* Températures non corrigées.

† Freund (7) donne 215° C. comme point de fusion du 4,4'-dinitro- α -cyanostilbène.

‡ et § Seul l'azote ou le chlore a été déterminé sauf pour ces deux composés dont l'analyse a donné respectivement les résultats suivants: Calc. C = 78.9; H = 5.7. Trouvé: C = 79.0; H = 6.2. Calc. C = 74.9; H = 6.2. Trouvé: C = 74.6; H = 6.7.

Dans deux cas, à savoir ceux de l' α -acétyl-4-nitrostilbène et de l' α -acétyl- β -chloro-4-phényldibenzyle, la gomme obtenue après la distillation à la vapeur au lieu d'être dissoute dans le chloroforme a été triturée à l'acide acétique et le solide cristallisé, la première substance de l'alcool à 95% (décoloration au noir animal) et la deuxième de l'acide acétique à 80% (décoloration au noir animal).

Acide α -chloro-4-chlorohydrocinnamique

L' α -chloro-4-chlorohydrocinnamitrile (4.8 g.) obtenu par la réaction de Meerwein a été hydrolysé par l'acide chlorhydrique concentré (50 ml.) à l'ébullition pendant 15 h. L'acide α -chloro-4-chlorohydrocinnamique cristallise de l'alcool éthylique à 20% en minuscules cristaux blancs de p.f. 98° à 100° C. Rendement 80%. Calculé pour $C_9H_8O_2Cl_2$: Cl, 32.4%. Trouvé: Cl, 32.0%.

Acide 4-chlorocinnamique

L'acide α -chloro-4-chlorohydrocinnamique (3 g.) est dissous dans la pipéridine (10 ml.). Il se produit un fort dégagement de chaleur. Après avoir porté à l'ébullition on refroidit, on dilue à l'eau et on filtre. L'acide cristallise de l'alcool éthylique à 50% en petits prismes blancs de p.f. 248° à 250° C. (cf. Gabriel et Herzberg (8) p.f. 240° à 242° C.). Rendement quantitatif. Calculé pour $C_9H_7O_2Cl$: Cl, 19.45%. Trouvé: Cl, 19.8%.

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Les auteurs désirent exprimer leur gratitude au Conseil National des Recherches pour un octroi et une Bourse de Recherches accordée à l'un d'eux (C.-A.O.) ainsi que pour la permission de publier ces résultats.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL
XXXII. 2,3-BUTANEDIOL FERMENTATIONS AT POISED HYDROGEN
ION CONCENTRATIONS¹

BY A. C. NEISH² AND G. A. LEDINGHAM²

Abstract

The anaerobic dissimilation of glucose by *Bacillus polymyxa*, *Bacillus subtilis* (Ford's type), *Aerobacter aerogenes*, and *Serratia marcescens* was studied at poised hydrogen ion concentrations covering the range pH 5.0 to 8.0. Each fermentation was controlled within ± 0.05 pH units by automatic addition of ammonium hydroxide solutions. The hydrogen ion concentration had a marked effect on the overall rate of dissimilation and the relative yield of products that was similar for all organisms. The time required to completely ferment a medium containing 5% glucose varied from 22 hr. for *Bacillus subtilis* to 9½ hr. for *Aerobacter aerogenes* at the optimum pH, which was within the range 7.0 to 7.6. The yield of 2,3-butanediol decreases above pH 6.4, until above pH 7.6 little or none is formed, although fairly rapid breakdown of glucose is still obtained. At the same time the yield of acetoin tends to increase, while there is little change in the amount of ethanol formed. The yields of acetic and lactic acids increase markedly in alkaline media, the latter showing an optimum at pH 7.6. A pronounced decrease in the yields of carbon dioxide and hydrogen occurs above pH 7.0 and is accompanied by an approximately equal increase in the yield of formic acid, which rises from 0.3 to 120 millimoles per 100 millimoles of glucose dissimilated in the *A. aerogenes* fermentation.

Introduction

Fermentation of carbohydrates by the 2,3-butanediol producing bacteria always yields some organic acids that will inhibit the growth of the organism if allowed to accumulate. To obtain complete fermentation of reasonably large amounts of carbohydrates, i.e., 3% or more, it is necessary to neutralize these acids as they are formed. This is usually accomplished by addition of an excess of calcium carbonate to the medium, which maintains the pH reasonably constant in the range 5.6 to 5.8.

Buffers such as phosphates are not practicable because such large amounts are involved that their concentration has to be too high. Consequently, studies of the effect of pH on the butanediol fermentation have been made by adding a strong base, such as sodium hydroxide, manually from time to time to keep the hydrogen ion concentration within a certain range. In this way, Mickelson and Werkman (9) were able to show that fermentation of glucose by *Aerobacter indologenes* gave more formic and acetic acids and less butanediol when the fermentations were run above pH 6.3 than when they were run in more acidic solutions. A similar effect has been observed with *Bacillus polymyxa* (1) and *Bacillus subtilis* (12). In these experiments, close control of the pH was not possible, and it may have varied by as much as

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as paper No. 73 on the Industrial Utilization of Wastes and Surpluses and as N.R.C. No. 1974. Presented to the Chemical Institute of Canada Convention at Halifax, N.S., June 1949.

² Present address: Prairie Regional Laboratory, Saskatoon, Sask., Canada.

2 pH units. The present paper describes results in which the pH was controlled within ± 0.05 pH units, by using an electronic pH monitor giving automatic control (3).

Although close control of the hydrogen ion concentration has not been tried previously on butanediol fermentations as far as the authors know, laboratory apparatus for automatic pH control of bacterial fermentations has been used before. Longworth and McInnes (6, 7, 8) have devised an apparatus giving automatic control of pH of bacterial fermentations and have studied the rate of formation of acids by *Lactobacillus acidophilus*. A similar apparatus has recently been described by Kepes (5).

Experimental

Organisms Used

Bacillus polymyxa, Strain No. C-2(1). This strain was isolated from soil in the Ottawa laboratories of the National Research Council.

Bacillus subtilis (Ford's Type) Strain No. 44, used in previous work (2).

Serratia marcescens, Strain No. S 16. This was obtained from Prof. B. Eagles at the University of British Columbia where it was designated as *Serratia F. V.*

Aerobacter aerogenes, Strain M 148. This was isolated from soil at the Ottawa laboratories of the National Research Council.

Preparation of Inoculum and Medium

The inoculum was prepared by transferring the organism from an agar slant into 10 ml. of a medium containing glucose (1%) and yeast extract (0.5%). It was then incubated for 24 hr. at the temperature to be used in the experiment. The fermentation medium contained glucose (5%), yeast extract (0.5%), potassium dihydrogen phosphate (0.05%), potassium monohydrogen phosphate (0.05%), and magnesium sulphate (0.02%). Each fermentation was run using 250 ml. of medium in a modified 1 liter Erlenmeyer flask (described below). The glucose (12.500 gm.) was autoclaved with 150 ml. of distilled water in the fermentation flask; the yeast extract and salts were sterilized separately, each in 50 ml. of distilled water. These solutions were added aseptically to the fermentation flask after cooling to room temperature. The purest grades of glucose and salts commercially available were used; the yeast extract was a Difco preparation.

Fermentation Apparatus

The electronic pH monitor, shaking apparatus, and the metering pump have been previously described by the inventors (3). The monitor was found to be quite reliable and it fills a long-felt need for a rugged, accurate, and dependable apparatus for laboratory control of the pH of fermenting solutions.

The fermentation flask and electrodes used in this investigation are shown in Fig. 1. The flask is a modified 1 liter Erlenmeyer provided with gas inlet (A) and outlet (B) tubes, an alkali inlet (E), an inoculum inlet (F) and two standard taper joints for insertion of the electrodes. The glass electrode (D) is a Leeds and Northrup Std. 1199-12 and is mounted in a standard taper 24/40 joint by a rubber tube connection as shown in Fig. 1. The calomel electrode and potassium chloride bridge are Leeds and Northrup Std. 1199-23-A and Std. 1199-27-A respectively. The reservoir is removed from the potassium chloride bridge and the 12 mm. diam. Pyrex tube containing the porous ring seal is fused to a standard taper 24/40 joint to give the calomel electrode assembly (C) shown in Fig. 1. The glass electrode and salt bridges are all of the same length from the top of the ground joint downwards (172 ± 2 mm.), so they are interchangeable, from one flask to another. The train used for purifying the gases and for the adsorption of the fermentation gases is similar to that previously used (10). Temperature control was achieved within ± 0.2 degrees Centigrade by placing the fermentation shaker in a constant temperature room.* The monitor, as well as the trains for purifying and absorbing the gases, was outside this room. The electrode leads and gas inlet and outlet tubes passed through holes in the wall.

Sterilization of the Electrodes and Accessory Equipment

In early work, the electrodes were sterilized chemically with mercuric chloride or hydrochloric acid and then washed in sterile distilled water. This rather lengthy procedure has been replaced by the use of germicidal light. The electrodes are now sterilized in the apparatus shown in Fig. 2. This is

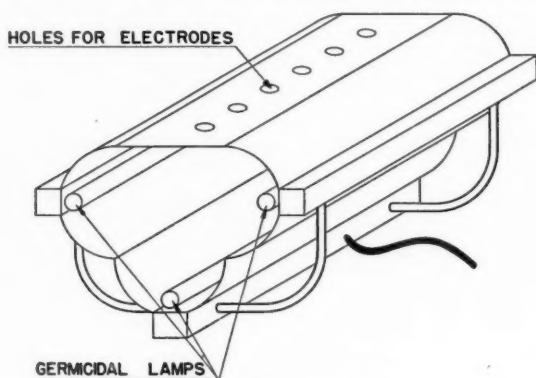


FIG. 2. Apparatus for sterilizing electrodes by ultraviolet light.

an aluminum box with three 18 in. germicidal lights mounted, one on each side and one on the bottom. The holes in the top are adjusted so a 24/40 S.T. joint is arrested after entering the hole about half way. The electrodes

* An early model of the shaker not having built-in temperature control was used in these studies.

PLATE I

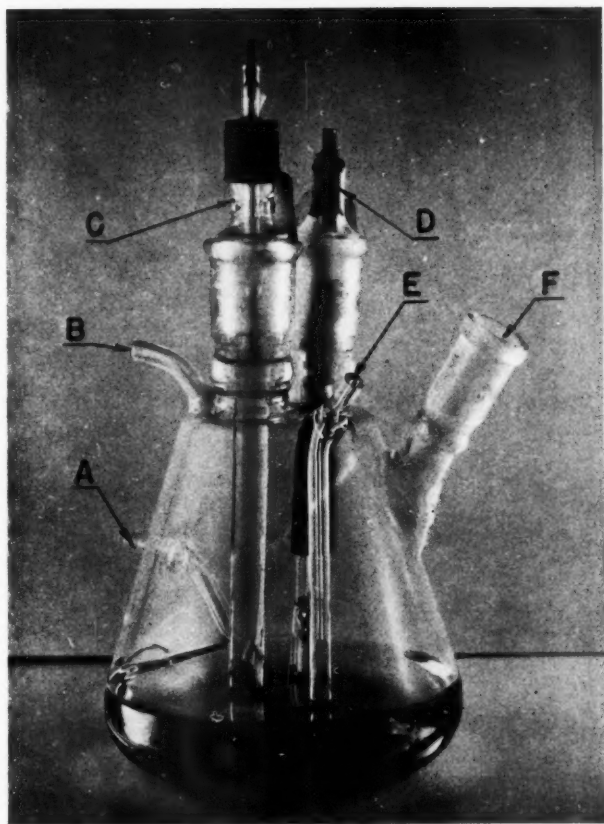
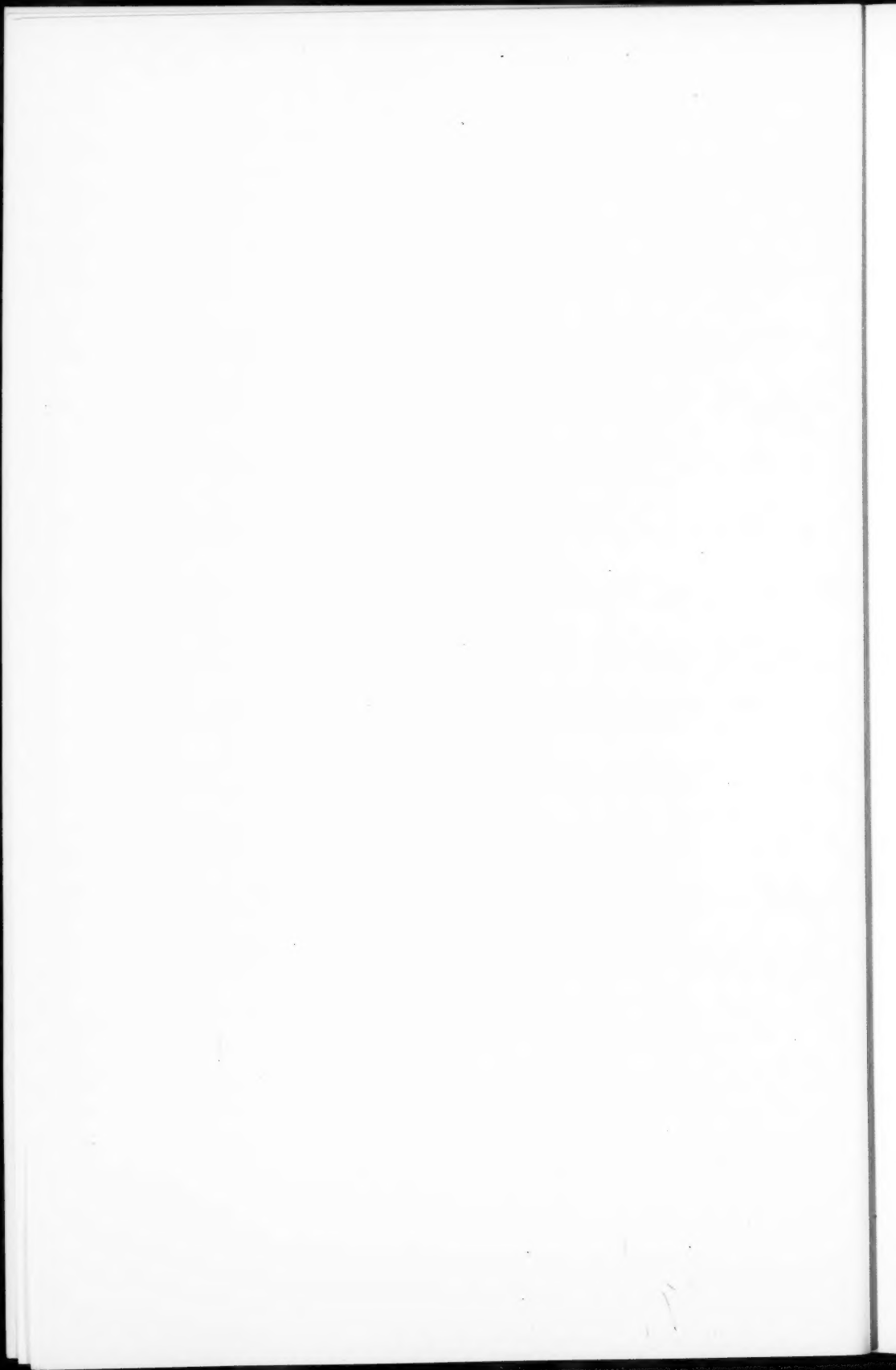


FIG. 1. *Flask and electrodes used in studies of pH controlled fermentations.*



are removed from the distilled water, in which they are usually stored, and inserted in these holes. After an irradiation period of 10 min. they are rotated through 90 degrees and then after 10 min. more they are removed and inserted quickly into the fermentation flask. This treatment has been found to sterilize electrodes that have been immersed in a thick sporulating suspension of *Bacillus subtilis*. The burettes used as alkali reservoirs with their connecting tubes are sterilized in the autoclave. The alkali is prepared by diluting concentrated ammonium hydroxide with sterile water.

Procedure for Starting the Fermentations

The inoculum, sterile medium, and sterile alkali are prepared the day before the fermentation is to be started and the potential of the electrodes measured in a buffer at the pH and temperature to be used in the experiment in order to obtain the correct potentiometer settings. The electrodes are sterilized by ultraviolet light as described above and transferred quickly to the fermentation flasks, which are placed directly in front of the sterilizer. The ground glass joints are then raised slightly and daubed with sterile grease to ensure a gas-tight connection. The flasks are then placed in the shaker of the fermentation apparatus and the electrodes and the gas inlet and outlet tubes are connected to the rest of the system. The alkali inlet tubes are then connected, care being taken first, to displace the air from the rubber tube by drawing off 10 ml. of alkali. The medium is allowed to shake for about half an hour until its temperature reaches that of the incubator and the pH then adjusted to the desired value by addition of sterile ammonium hydroxide through the pump, or of sterile hydrochloric acid (2 *N*) from a medicine dropper through the inoculum inlet. The strength of the ammonium hydroxide solution used is governed by the pH of the fermentation. Large amounts are required for fermentations run at pH's above 7, and 4 *N* base is usually used. For pH's between 6 and 7, 2 *N* base is employed, while for fermentations below pH 6, 1 *N* base is preferable.

While the pH is being adjusted, the metering pumps are also adjusted to deliver approximately 0.3 ml. per min. The inoculum then is poured aseptically into the fermentation flask through the neck provided for that purpose. The final adjustment of the pH is now made and the inoculum inlet is closed by means of a ground-glass stopper treated with sterile grease to give a gas-tight seal. The alkali burettes are now filled. These burettes are read from time to time during the fermentations in order to follow the rate of acid formation. Variations of the pH of the medium are recorded by a recording milliammeter connected to the pH monitor. When the fermentation is finished, acid production stops owing to disappearance of the glucose, and the medium usually becomes alkaline, possibly because of the action of amino acid decarboxylases. One or two hours is allowed, to make sure the fermentation gases have been swept out, the new balance point is measured, and a 50 ml. sample of the medium is then taken and its pH measured on an independent instrument. This is done to make sure

there has been no drifting of the potential of the electrodes in the fermentation flask. A small sample is taken for bacteriological examination at this stage. Repeated tests have failed to show the presence of any contaminants. The electrodes are removed from the fermentation flask and replaced with rubber stoppers. The 50 ml. sample is returned to the fermentation flask quantitatively and a 50% excess of 5 *N* hydrochloric acid poured from a graduated cylinder through the inoculum inlet, which is quickly stoppered, and the medium then swept out for a period of three hours or more, with shaking to remove the dissolved carbon dioxide formed by decomposition of carbonates. The electrodes are washed by dipping them several times in distilled water; they are then stored in distilled water.

Analysis of Fermented Solutions

The fermented solution is mixed with the contents of the cold trap and then cleared with zinc hydroxide as described previously (10), the only difference being that the solutions are now made up to 500 ml. The analyses are conducted as before, except for improvements in the determination of the acids and the carbon assimilated. The acids are now determined by a method based on partition chromatography (11). The carbon assimilated is determined using the manometric method of Van Slyke and Folch (13). This determination is made on a fraction representing the carbon precipitated by zinc hydroxide plus the carbon in nonvolatile compounds *not* extracted by ether from neutral or acidic aqueous solutions. This fraction is obtained by combining the thrice-washed zinc hydroxide precipitate with an equivalent amount of the aqueous solution obtained after extraction of the neutral products and acids by ether. A fraction representing one-tenth of the total fermentation solution is made up to 200 ml. and a 5 ml. aliquot of the thoroughly mixed suspension is pipetted into the combustion tube. It is then dried in a vacuum desiccator and analyzed by the macro method (13). The carbon found is corrected for any glycerol or residual sugar in the fermented solution. A blank determination is made on a solution containing the same amount of yeast extract as the fermentation medium. When further corrected for this blank the carbon is taken to be the glucose carbon assimilated by the micro-organisms, since all the fermentation products, except glycerol, are either extracted by ether or volatilized.

Results and Discussion

Carbon balances showing the effect of variation of pH on the anaerobic dissimilation of glucose by *B. polymyxa*, *A. aerogenes*, *S. marcescens*, and *B. subtilis* are shown in Tables I, II, III, and IV respectively. Because of the similarity of the results obtained, these tables will be considered collectively.

The over-all rate of glucose dissimilation at the optimum hydrogen ion concentration is some three to six times as fast as that previously found with these organisms in calcium carbonate buffered media. It was found that the

TABLE I

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Bacillus polymyxa*

All fermentations were incubated at 30° C. using a medium containing 5.0% glucose and 0.5% yeast extract. The pH was controlled by automatic addition of ammonium hydroxide while anaerobic conditions were maintained by bubbling purified nitrogen through the medium.

Product	pH 5.40	pH 5.80	pH 6.20	pH 6.47	pH 6.80	pH 7.17	pH 7.60
	Millimoles per 100 millimoles of glucose dissimilated						
2,3-Butanediol	43.3	51.3	50.5	49.7	44.2	33.2	11.3
Acetoin	2.32	1.77	2.36	1.88	3.48	2.88	4.90
Ethanol	67.4	71.4	73.1	69.3	67.3	75.0	78.9
Glycerol	2.90	3.39	2.84	2.24	3.23	2.02	2.39
Acetone	2.23	0.34	0.38	0.21	Nil	0.33	Nil
Butyric acid	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Acetic acid	1.85	2.11	3.15	6.32	16.59	26.45	46.7
Formic acid	0.47	0.22	2.76	1.61	3.56	4.81	82.6
Succinic acid	1.68	0.79	0.64	0.21	1.67	6.65	4.45
Lactic acid	0.75	1.67	2.12	1.67	1.84	3.20	6.52
Carbon dioxide	183.9	186.5	183.1	187.1	175.3	161.2	78.9
Hydrogen	89.2	68.0	70.4	78.0	84.1	82.1	46.0
Glucose carbon assimilated	32.8	—	—	—	31.9	—	29.6
Fermentation time, hr.	53	30	26	26	26	28	53
% glucose used*	99.6	100.0	100.0	100.0	100.0	99.9	9.44
% carbon accounted for	93.9	94.1	94.8	93.5	98.8	95.0	91.6
O/R index	1.01	1.00	0.97	1.01	0.99	0.98	0.99

* Determined by direct estimation of the glucose before and after fermentation.

TABLE II

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Aerobacter aerogenes*

Fermentations run under the same conditions as for *B. polymyxa* (Table I)

Product	pH 5.00*	pH 5.00	pH 5.20	pH 5.60	pH 6.00	pH 6.60	pH 7.00	pH 7.60	pH 8.00
	Millimoles per 100 millimoles of glucose dissimilated								
2,3-Butanediol	40.2	38.7	48.8	47.9	47.5	38.8	10.78	Nil	Nil
Acetoin	2.43	2.46	1.39	2.39	1.58	2.10	3.08	3.85	5.82
Ethanol	56.4	60.5	61.2	56.3	57.4	55.2	57.7	54.7	60.9
Glycerol	4.13	2.22	1.81	3.91	3.34	4.37	5.79	7.72	6.55
Acetone	Nil	Nil	0.53	Nil	0.07	Nil	Nil	Nil	Nil
Butyric acid	1.07	0.59	0.29	0.07	Nil	0.44	0.68	1.79	3.95
Acetic acid	23.7	20.8	3.89	4.23	7.96	12.95	42.3	52.7	52.6
Formic acid	0.50	0.26	0.43	0.36	0.77	0.44	22.5	52.4	119.6
Succinic acid	1.25	1.29	2.17	2.04	1.80	3.08	6.19	4.10	9.29
Lactic acid	3.15	3.49	2.34	2.64	3.35	7.59	25.0	36.5	9.80
Carbon dioxide	188.0	190.5	183.8	171.1	174.0	167.0	106.8	77.4	19.60
Hydrogen	98.9	103.0	69.8	57.6	74.2	80.7	81.4	69.7	10.37
Glucose carbon assimilated	—	37.6	42.5	66.2	65.1	93.0	87.6	53.2	83.1
Fermentation time, hr.	143	142	94	29½	14½	10½	10	9½	21
% glucose used	65.5	68.0	99.9	100.0	100.0	100.0	100.0	99.9	93.4
% carbon accounted for	91.1	96.9	97.0	97.9	99.0	101.8	98.6	94.9	95.9
O/R index	1.10	1.10	1.07	1.06	1.03	1.06	1.00	1.07	1.07

* Duplicate runs were made at pH 5.00 because the sudden increase in acetic acid and hydrogen was unexpected and needed confirmation.

TABLE III

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Serratia marcescens*Fermentations run under the same conditions as for *B. polymyxa* (Table I)

Products	pH 6.40	pH 6.80	pH 7.20	pH 7.60	pH 7.80
	Millimoles per 100 millimoles of glucose dissimilated				
2,3-Butanediol	55.2	49.4	30.1	2.48	Nil
Acetoin	1.58	1.87	3.99	6.21	5.87
Ethanol	46.7	49.9	49.5	49.3	41.0
Glycerol	2.16	6.78	2.79	2.44	9.61
Acetone	Nil	0.13	Nil	Nil	Nil
Butyric acid	Nil	0.24	Nil	1.49	1.49
Acetic acid	1.90	6.32	28.2	51.8	49.0
Formic acid	45.7	59.2	85.6	113.5	91.4
Succinic acid	2.86	4.35	7.52	5.81	4.75
Lactic acid	9.66	8.81	18.21	61.6	64.8
Carbon dioxide	116.1	106.5	53.1	2.76	2.16
Hydrogen	0.78	0.16	0.49	1.81	0.15
Glucose carbon assimilated	63.9	46.6	59.1	61.5	38.1
Fermentation time, hr.	94	31	21	34	40
% glucose used	94.9	100.0	99.9	100.0	99.9
% carbon accounted for	99.4	98.8	97.1	102.5	98.0
O/R index	1.06	1.07	0.99	1.06	0.95

TABLE IV

ANAEROBIC DISSIMILATION OF GLUCOSE BY *B. subtilis* (FORD'S TYPE)

Products	pH 6.00	pH 6.20	pH 6.40	pH 6.60	pH 6.80	pH 7.20	pH 7.60	pH 8.00
	Millimoles per 100 millimoles of glucose dissimilated							
2,3-Butanediol	36.8	39.5	32.3	27.7	20.8	17.65	11.82	Nil
Acetoin	1.31	2.65	0.99	2.89	2.37	1.44	2.99	2.10
Ethanol	20.51	15.05	13.81	15.10	20.2	20.4	22.3	36.9
Glycerol	29.9	31.1	33.5	19.81	18.99	12.61	10.32	17.00
Butyric acid	0.17	0.32	0.46	0.86	0.98	0.89	2.38	1.30
Acetic acid	0.87	1.16	0.74	2.24	2.36	7.44	12.81	49.5
Formic acid	12.38	16.57	11.52	19.00	17.63	27.6	39.6	96.0
Succinic acid	1.08	0.73	0.82	0.98	1.12	0.89	2.24	4.56
Lactic acid	41.4	65.6	70.9	97.1	95.0	106.7	119.0	54.1
Carbon dioxide	91.4	86.4	80.6	60.2	59.6	40.0	32.4	3.47
Hydrogen	0.38	0.48	0.16	1.81	0.49	0.23	0.33	0.78
Glucose carbon assimilated	82.1	15.8	15.2	33.4	28.4	25.3	22.6	21.2
Fermentation time, hr.	71	87	62	31	32	22	23	47
% glucose used	85.2	97.9	100.0	100.0	100.0	100.0	100.0	94.7
% carbon accounted for	100.0	102.0	98.0	104.3	100.3	98.3	105.0	92.8
O/R index	1.06	1.08	1.08	0.98	1.07	0.98	1.05	1.09

optimum rate of glucose dissimilation occurred in neutral or slightly alkaline media (see Fig. 3). It is interesting to note that these bacteria vary considerably in their sensitivity to changes in pH. The rate of glucose dissimilation by *A. aerogenes* and *B. polymyxa* is nearly constant over quite a

wide pH range, while the other two species have a rather sharp optimum due chiefly to their inhibition in acid solutions. The increased rate obtained at a favorable hydrogen ion concentration is partly due to an increased population

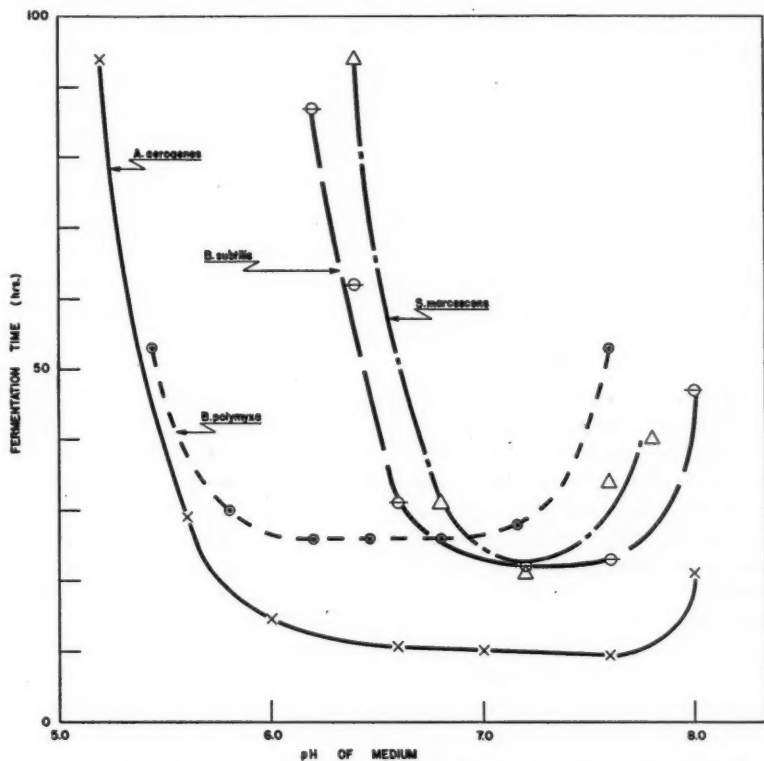


FIG. 3. Effect of pH on rate of dissimilation of glucose. The fermentation time is that required for complete fermentation of the glucose (5% concentration).

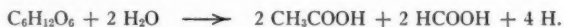
of bacteria. Accurate counts of the numbers of bacteria per unit volume were not made, but mere visual inspection of the turbidity shows that at the optimum pH greatly increased growth is obtained. Longworth and MacInnes (8) found that *Lactobacillus acidophilus* gave a fourfold increase in growth and a ninefold increase in acid production when grown at pH 6.0, compared to the increase in a culture grown without control of the acidity. It would be interesting to study the effect of pH on the kinetics of sugar breakdown by the 2,3-butanediol bacteria, and to relate the rate of fermentation with the numbers of viable and total cells.

Variation of the hydrogen ion concentration caused a marked variation in the relative yields of products. This is especially striking with 2,3-butanediol, the yield decreasing markedly above pH 6.4, until above pH 7.6 little or

none is formed. At the same time the acetoin tends to increase. It must be remembered that these figures are relative yields, and one reason for the decrease of 2,3-butanediol is failure for its production to increase as rapidly as that of other products, such as lactic acid, when the pH is increased. For example, *A. aerogenes* is producing 2,3-butanediol at approximately twice as fast an absolute rate at pH 7.0 when 10.8 millimoles are produced in 10 hr. as at pH 5.2 when 49 millimoles are produced in 94 hr., yet the relative yield at pH 7.0 is less than one-quarter that at pH 5.2. If a homo-fermentative strain, forming 2,3-butanediol, could be obtained it might give its best fermentation at about pH 7.0.

In general the acids are formed in greatest amounts in alkaline media. Lactic acid is formed in optimum yield at pH 7.6. The yield of acetic acid passes through a minimum at pH 5.2 with *A. aerogenes* (see Table II), more than five times as much being made at pH 5.0, but the best yields are obtained above pH 7.0. It was not possible to demonstrate this minimum with the other organisms, since they do not ferment rapidly enough at pH 5.0 to make the experiments practicable.

One of the most striking changes is the large increase in formic acid formation that occurs with *B. polymyxa* and *A. aerogenes*. These organisms produce only traces of this acid in acidic media but it is one of the major products in alkaline media. For example *A. aerogenes* produces almost 120 millimoles for every 100 millimoles of glucose fermented at pH 8.0, while at pH 5.0 to 6.6 less than 0.5 millimole is formed. Concomitant with this large increase in formic acid there is an almost equally large decrease in the yields of carbon dioxide and hydrogen. This suggests that these organisms normally produce hydrogen in acidic media by enzymic decomposition of formic acid but when they are grown in alkaline media formic acid accumulates owing to inhibition of this reaction. Even with the other organisms that never produce much hydrogen (Tables III and IV) there is an increase in the amount of formic acid in alkaline media, while the production of carbon dioxide may fall to only 2 to 3 millimoles for each 100 millimoles of glucose dissimilated. This decrease is partly due to increase in the lactic acid fermentation, which does not yield carbon dioxide, and is partly due to the accumulation of formic acid. In general, these four species can all be considered to carry out the following over-all reaction in alkaline medium.



The four hydrogen atoms produced in this reaction could then be used to produce more formic acid by other reactions such as:



The carbon balances in this paper are in agreement with this hypothesis. It is difficult to explain why formic acid should be obtained by several different reactions unless the enzyme systems or carriers responsible for eliminating carbon dioxide from the cell are functioning at a greatly reduced rate.

Succinic and butyric acids, though never produced in very large amounts, show an increased yield in alkaline media. The yield of ethanol is not affected much by variation in the hydrogen ion concentration. The yield of glycerol is changed somewhat and seems to pass through a minimum at pH 7.6 (see Table IV).

To obtain good carbon recoveries it is necessary to determine the carbon assimilated, since as much as 15% of the glucose carbon may be found in this fraction. It will be noted that the redox balances are usually somewhat in excess of the theoretical value of 1.00. This is to be expected since the glucose carbon assimilated must be partly synthesized to compounds such as fats and protein, which are more reduced than glucose, yet these were not considered in working out the redox balance owing to uncertainty regarding the magnitude of the negative value to use in calculating their contribution.

Although the results of this investigation have been discussed in terms of the effect of variation of the hydrogen ion concentration on the rate of the fermentations and yields of products, it must be remembered that hydrogen ions may have an indirect effect. These changes may be caused by variation in the amounts of undissociated organic acids (8), ammonium ions, or undissociated ammonium hydroxide, since these vary in concentration as the hydrogen ion concentration is varied. Furthermore, whatever the causative agent may be, it need not act directly on the enzymes of mature cells but may affect growing cells in such a way that production of certain enzymes is inhibited. The latter effect has been demonstrated by Brewer, Mickelson, and Werkman (4) for *Aerobacter indologenes*. They found that the nature of the enzymic activity of nonproliferating cells on glucose in both acid and alkaline buffers depends on the nature of the medium in which the cells are grown. Cells grown in acid glucose media produced more 2,3-butanediol than cells grown in alkaline media whether tested in acid or alkaline glucose solution although more was produced in the acid test media. However, although the best yield of formic acid was obtained in an alkaline glucose solution, it was obtained using cells originally grown in an acid glucose medium. Hence this type of adaptation will not completely explain the results of the present investigations: it is necessary also to postulate an effect on the fermentation apparatus of mature cells.

Since hydrogen ions enter into many biological oxidation-reduction reactions one can expect the redox potential to depend on the pH of the medium. Although it is not yet certain what the apparent redox potential of a fermentation signifies it should be very instructive to examine the relation between pH and eH with the 2,3-butanediol bacteria.

Acknowledgment

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POLYVINYL NITRATE¹

By S. A. V. DEANS² AND R. V. V. NICHOLLS

Abstract

Existing methods of nitration of polyvinyl alcohol involving the use of fuming nitric acid alone, or mixtures of fuming nitric acid and sulphuric acid, have been modified to give products improved in nitrogen content, color, and yield. A method involving the use of fuming nitric acid and acetic anhydride has been developed. The explosive characteristics of polyvinyl nitrate of various degrees of polymerization prepared by five different methods are reported.

Introduction

The hydroxyl groups in polyvinyl alcohol tend to react in the same manner as the hydroxyl groups present in simple alcohols. In particular they are capable of being esterified to form polyvinyl esters. Organic esters of polyvinyl alcohol are well known but the nitrate is the only inorganic ester of polyvinyl alcohol that has been prepared:



In general, esters of nitric acid, such as the alkyl nitrates, nitroglycerine, nitrostarch, and nitrocellulose, possess explosive properties. Polyvinyl nitrate is no exception.

Frank and Kruger (5) found that the methods of nitration customarily employed for glycerol, starch, and cellulose were not applicable to polyvinyl alcohol. In order to reduce the tendency for oxidation to occur, they dissolved the polyvinyl alcohol in sulphuric acid and added the solution to a nitrating mixture containing excess sulphuric acid. Polyvinyl nitrate was obtained in the form of pale yellow plastic granules, the yield being 80%. The product contained 10% nitrogen, the maximum theoretical value being 15.7%. It could be detonated either by heat or shock.

Burrows and Filbert (2, 3) showed that finely powdered polyvinyl alcohol tended to float on the surface of fuming nitric acid where it would ignite and continue to burn in contact with the air. When the polyvinyl alcohol was finally immersed in the nitrating acid, the reaction was so rapid that the material was largely oxidized. To avoid this side reaction, the powdered polyvinyl alcohol was first mixed with enough water to render it moist and

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² Holder of a Bursary, a Studentship, and a Fellowship under the National Research Council of Canada. At present: Process Development Chemist, Ayerst, McKenna and Harrison, Montreal, Quebec.

cohesive. It was then grained through a 30 mesh screen and dried. It was found that this grained material could be more readily immersed beneath the surface of the nitrating acid, and thus the tendency for oxidation to occur was reduced to a minimum. The temperature was maintained at 15° to 20° C. and the syrupy orange-red solution thus obtained was poured into cold water, the polyvinyl nitrate precipitating as a cream-colored powder in 80% yield. The product contained 13.8% nitrogen, the maximum theoretical value being 15.7%. With less concentrated nitric acid, the polyvinyl nitrate was obtained in smaller yield and the product possessed a lower nitrogen content.

In the present investigation a detailed study of the preparation of polyvinyl nitrate was carried out. The addition of powdered polyvinyl alcohol to fuming nitric acid alone, to fuming nitric acid - acetic anhydride mixtures, and to fuming nitric acid - fuming sulphuric acid mixtures gave rise to polyvinyl nitrate. Furthermore, the addition of an acetic anhydride suspension of polyvinyl alcohol to fuming nitric acid - acetic anhydride mixtures and to fuming nitric acid - fuming sulphuric acid mixtures also gave rise to polyvinyl nitrate. These five methods were applied to polyvinyl alcohol of various degrees of polymerization.

The tests on polyvinyl nitrates of various degrees of polymerization as obtained by these five different methods of preparation included the softening point, the Trauzl lead block test, the impact test, the ignition test, and the Abel heat test.

Experimental Procedures

1. PREPARATION OF POLYVINYL ALCOHOLS

Polyvinyl acetates of various degrees of polymerization were obtained from Shawinigan Chemicals Ltd.*, Shawinigan Falls, Que., and were converted into polyvinyl alcohols. The yields and residual-acetate contents are presented in Table I. The polyvinyl alcohol was prepared by adding a methanolic

TABLE I
CONVERSION OF POLYVINYL ACETATE INTO POLYVINYL ALCOHOL

Polyvinyl acetate Average degree of polymerization (No. of structural units)	Polyvinyl alcohol	
	Yield, %	Residual acetate, mole %
30	87.3	0.60
70	93.2	0.63
150	93.8	0.89
230	93.8	1.21
350	95.4	1.47
700	97.7	1.68

* We wish to acknowledge several donations of generous samples of these polymers.

solution of polyvinyl acetate to a dilute methanolic solution of sodium methoxide.* It will be observed that the yield and residual acetate content of the polyvinyl alcohol increased with an increase in the degree of polymerization of the polyvinyl acetate from which it was formed.

The polyvinyl alcohols were converted into polyvinyl nitrates by a variety of methods. The original intention was to observe the effect of variation in the chain length on the explosive characteristics of the polyvinyl nitrate.

2. PREPARATION OF POLYVINYL NITRATES

1. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid*

In a 500 cc. round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a small solids funnel was placed 200 cc. of fuming nitric acid (95%). Exactly 15 gm. of polyvinyl alcohol, reduced to a fine powder by means of a ball mill, was added through the funnel in small portions over a period of 30 min. with efficient stirring, the reaction mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the yellow solution was poured into a well stirred mixture of 1000 gm. of ice and water in order to precipitate the polyvinyl nitrate.

In the case of polyvinyl alcohols of very high degree of polymerization it was found advantageous to employ somewhat larger amounts of fuming nitric acid since the viscosity of the resultant solution was high.

It should be noted that by carrying out the nitration at -10° to -5° C. there was no tendency for powdered polyvinyl alcohol to ignite even though it floated on the surface of the nitrating acid in contact with the air for several seconds.

The form of the product depends on its degree of polymerization. Polyvinyl nitrates of low degree of polymerization precipitated in the form of a white powder. Polyvinyl nitrates of high degree of polymerization, on the other hand, tended to coagulate in the form of tough white strands, thus giving rise to a bulky material. In either case, the mixture was filtered with suction and the product washed with water until the filtrate was neutral to litmus.

The purification of polyvinyl nitrate could be effected in a satisfactory manner only when the product was obtained in the form of a powder. In order to remove any impurities occluded by the small particles of polyvinyl nitrate, the latter was ground in a ball mill in the presence of 300 cc. of water for a period of 12 hr. The suspension of polyvinyl nitrate thus obtained was filtered with suction and the product washed with water until free of acid. The purification procedure was repeated to ensure complete removal of impurities. The product was then dried by exposure to the air.

On the other hand, when polyvinyl nitrate was obtained in a bulky form, it could not be ground in the ball mill and was therefore allowed to soak in

* The use of sodium methoxide was recommended by Dr. D. McIntosh, Shawinigan Chemicals Ltd., Shawinigan Falls, Quebec.

water for a period of two days after which it was filtered and allowed to dry by exposure to the air.

2. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid - Acetic Anhydride Mixtures.*

In a 400 cc. beaker equipped with a mechanical stirrer and a thermometer was placed 100 cc. of technical acetic anhydride. The beaker was maintained at a temperature of -10° to -5° C. and 100 cc. of fuming nitric acid (95%) was slowly added. Exactly 15 gm. of polyvinyl alcohol, reduced to a powder by means of a ball mill, was added to small portions over a period of 30 min. with efficient stirring, the reaction mixture being maintained at -10° to -5° C. throughout the experiment. The polyvinyl nitrate was thus obtained as a fine suspension in the nitrating acid. Stirring was continued for another hour in order to complete the nitration.

It was possible to obtain the polyvinyl nitrate by filtration but the product tended to coagulate, thus forming an elastic mass that could not be readily purified. Instead, therefore, the suspension of polyvinyl nitrate was poured into a well stirred mixture of 1000 gm. of ice and water, thus precipitating the polyvinyl nitrate in the form of a white powder. The mixture was filtered with suction and the product washed until free of acid. It was then purified by grinding in a ball mill in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and drying by exposure to the air.

The present method was most suitable for polyvinyl alcohols of high degree of polymerization. In the case of polyvinyl alcohols of low degree of polymerization (below 150), however, the product, in suspension in the nitrating acid, tended to coagulate even when the stirring was very efficient, thus forming an elastic mass that could not be readily purified. It was possible to avoid this difficulty by using a larger quantity of nitrating acid but in the case of polyvinyl alcohols of very low degree of polymerization (e.g., 30) the product tended to coagulate as rapidly as it was formed.

Using fuming nitric acid - acetic anhydride mixtures, unlike the use of fuming nitric acid alone, there was no tendency for the polyvinyl alcohol to ignite on the surface of the nitrating acid even at room temperature. It was necessary to carry out the reaction at -10° to -5° C., however, since the tendency for the product to coagulate in the nitrating acid increases markedly above this temperature.

3. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid - Fuming Sulphuric Acid Mixtures.*

In a 400 cc. beaker equipped with a mechanical stirrer and a thermometer was placed 100 cc. of fuming nitric acid (95%). The beaker was maintained at -10° to -5° C. and 100 cc. of fuming sulphuric acid (free sulphur trioxide about 20%) was slowly added. Exactly 15 gm. of polyvinyl alcohol, reduced to a powder by means of a ball mill, was added in small portions from a spatula over a period of 30 min. with efficient stirring, the reaction mixture

being maintained at -10° to -5° C. throughout the experiment. The polyvinyl nitrate was obtained as a suspension in the nitrating acid. Stirring was continued another hour in order to complete the nitration.

As in the previous method of nitration, it was possible to obtain the polyvinyl nitrate by filtration of the suspension, but the product tended to coagulate to form an elastic mass that again could not be readily purified. Instead, therefore, the suspension of polyvinyl nitrate in nitrating acid was poured into a well stirred mixture of 1000 gm. of ice and water, the product precipitating in the form of a colored (buff to yellow) powder. The mixture was filtered by suction and the product washed until free of acid. It was purified by grinding it in a ball mill in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and drying by exposure to the air.

The present method, unlike previous ones, gave more colored products. A temperature of -10° to -5° C. was necessary since at higher temperatures the product tended to coagulate in the form of an elastic mass that then decomposed with liberation of brown fumes and deposition of a carbonaceous residue. It was effective for polyvinyl alcohols of high degree of polymerization only. In the case of polyvinyl alcohols of low degree of polymerization (below 230) the product, suspended in the nitrating acid, tended to coagulate even when the stirring was very efficient, thus forming an elastic mass that decomposed. It was possible to avoid this difficulty by using a larger quantity of nitrating acid but in the case of polyvinyl alcohols of very low degree of polymerization (e.g. 30) the product tended to coagulate and decompose as rapidly as it was formed.

4. By Adding an Acetic Anhydride Suspension of Polyvinyl Alcohol to Fuming Nitric Acid - Acetic Anhydride Mixtures

In a 1 liter round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a 500 ml. separatory funnel was placed 275 cc. of technical acetic anhydride. Then 275 cc. of fuming nitric acid (95%) was added with stirring at -10° C. A suspension of polyvinyl alcohol in acetic anhydride, prepared by grinding 50 gm. of polyvinyl alcohol in the presence of 300 cc. of technical acetic anhydride in a ball mill for 12 hr., was then added by means of a separatory funnel over a period of one hour with rapid stirring, the mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the suspension of polyvinyl nitrate thus obtained was immediately poured into 2000 gm. of ice and water with rapid stirring, the polyvinyl nitrate precipitating in the form of a white powder.

The mixture was filtered by suction and the product washed until free of acid. It was purified by grinding it in a ball mill in the presence of water to ensure complete removal of impurities and then drying the product by exposure to the air.

This method of preparation apparently may be applied to polyvinyl alcohols of any degree of polymerization, the product always being obtained in the form of a white powder. As in the method involving the addition of powdered polyvinyl alcohol to fuming nitric acid - acetic anhydride mixtures, there was no tendency for the polyvinyl alcohol to ignite on the surface of the nitrating acid even at room temperature. It was necessary to carry out the reaction at -10° to -5° C., however, since the tendency for the product to coagulate on the nitrating acid increased markedly above this temperature. Thus, for example, at 25° C., the polyvinyl nitrate coagulated in the form of an elastic mass on the stirrer almost immediately upon the addition of polyvinyl alcohol to the nitrating acid. On the other hand, at very low temperatures (-40° C.) the reaction rate was diminished and thus only a small yield of polyvinyl nitrate was obtained.

Alternatively, on adding an acetic anhydride suspension of polyvinyl alcohol to fuming nitric acid (95%) alone, the product at first tended to remain in solution in the nitrating acid but, on further addition of acetic anhydride suspension of polyvinyl alcohol, it precipitated in the form of an elastic mass that could not be readily purified.

5. *By adding an Acetic Anhydride Suspension of Polyvinyl Alcohol to Fuming Nitric Acid - Fuming Sulphuric Acid Mixtures*

In a 1 liter round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a 500 ml. separatory funnel was placed 300 cc. of fuming nitric acid. Then, 300 cc. of fuming sulphuric acid (free sulphur trioxide about 20%) was added slowly with stirring at -10° C. A suspension of polyvinyl alcohol in acetic anhydride, prepared by grinding 50 gm. of polyvinyl alcohol in the presence of 300 cc. of technical acetic anhydride in a ball mill for 12 hr., was then added by means of a separatory funnel over a period of one hour with rapid stirring, the mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the suspension of polyvinyl nitrate thus obtained was immediately poured into 2000 gm. of ice and water with rapid stirring, the polyvinyl nitrate precipitating in the form of a colored powder.

The mixture was filtered with suction and the product washed till free of acid. It was then purified by grinding it in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and then drying the product by exposure to the air.

This method of preparation may be applied to polyvinyl alcohols of any degree of polymerization, the product always being obtained in the form of a buff-colored powder. It was a poor method, however, since acetic anhydride and fuming sulphuric acid on mixing produced enough heat to cause decomposition of the product even when the stirring was very efficient and the mixture was maintained at -10° to -5° C.

3. PROPERTIES OF POLYVINYL NITRATE

In both the deacetylation of polyvinyl acetate to form polyvinyl alcohol and in the nitration of polyvinyl alcohol to form polyvinyl nitrate, fission of the polymeric chain may occur, thus giving rise to products of lower degree of polymerization than the original polyvinyl acetate. Throughout the discussion, however, it has been assumed for the sake of brevity that in a given preparation the degrees of polymerization of the polyvinyl acetate, polyvinyl alcohol, and polyvinyl nitrate are identical.

The nitrogen content of polyvinyl nitrate was determined by means of a Du Pont nitrometer (9, pp. 61-68). The nitrogen contents obtained for polyvinyl nitrate were in general between 13 and 15%, the maximum theoretical value being 15.73%.

The testing of polyvinyl nitrate as an explosive was carried out after the wetted samples had been dried at room temperature for a period of 36 hr. The actual tests* include softening point (1, p. 335), the Trauzl lead block test (8, pp. 104-106), the impact test, the ignition test, and the Abel heat test (6).

The softening point of polyvinyl nitrate was found to lie between 49 and 68° C. in all cases.

The Trauzl block values for polyvinyl nitrate varied from 153 to 341 cc. The value for standard trinitrotoluene obtained for purposes of comparison was found to be 255 cc.

In the impact test a small sample of polyvinyl nitrate was subjected to the shock of a falling weight (1780 gm.) in a Rotter Impact Machine, and the minimum height from which the weight had to fall in order to detonate the sample was noted. The value for standard trinitrotoluene, obtained for purposes of comparison, was 158 cm. The values obtained for polyvinyl nitrate varied from 30 to 335 cm. After these tests had been carried out, the samples were allowed to stand for a week. It was then found that the impact test gave much lower values, indicating increased sensitivity. This observation seemed to indicate that the polyvinyl nitrate was slowly decomposing.

The ignition test was performed by placing 0.02 gm. of polyvinyl nitrate in a test tube in a bath of Wood's metal at 100° C. and increasing the temperature at a rate of 20 degrees per minute until ignition occurred. The temperature at which brown fumes were evolved and the temperature at which ignition occurred were noted. The ignition point of polyvinyl nitrate in all cases was found to lie between 106° and 178° C.

The Abel heat test was carried out at 70° C. In all cases the values obtained were low as compared with, say, those of commercial cellulose nitrate with a heat test in excess of 10 min.

The properties of polyvinyl nitrate described above are set forth in detail in Tables II to VI.

* These tests were carried out by Mr. M. C. Fletcher, Chief Explosives Chemist, Department of Mines and Resources, Canada, whose assistance is acknowledged with gratitude.

TABLE II

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO FUMING NITRIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	89.0	14.8	—	341	86*	Nil	176	5	24
70	90.5	14.6	63	313	44	Nil	177	6	8
150	85.7	14.9	—	316	52	Nil	170	3	3
230	90.5	15.0	—	223‡	36	164	170	1	10‡
350	93.0	14.9	—	211‡	30	167	172	1	15‡
700	92.2	14.9	—	178‡	30	173	178	1	23‡

* Value obtained for impact test six days later = 28 cm.

† Density of bulky polyvinyl nitrate as fired in lead block = 0.20 gm. per cc.

‡ Weight of bulky polyvinyl nitrate as used in Abel heat test = 1 gm.

TABLE III

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND ACETIC ANHYDRIDE

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
70	84.5	14.5	60	312	76	173	173	1	50
150	85.7	14.3	—	308	62	170	172	0	48
230	89.0	14.4	—	300	62	155	164	0	43
350	87.4	13.9	—	288	42	150	170	0	35
700	92.2	14.4	—	300	104	165	173	0	58

TABLE IV

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND FUMING SULPHURIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
70	88.5	14.2	59	280	44	122	122	1	48
150	89.0	14.9	—	230*	42	170	170	1	33
230	89.0	14.4	—	310	38	138	162	1	20
350	87.4	14.5	—	303	54	122	126	1	5
700	85.7	14.2	—	288	30	122	122	1	8

* The lead block test was carried out on 3.8 gm. of polyvinyl nitrate and calculated to 10 gm. basis.

TABLE V

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF ACETIC ANHYDRIDE SUSPENSION OF POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND ACETIC ANHYDRIDE

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	90.8	14.7	68	318*	335-Neg.	160	176	1	25
70	91.1	14.9	63	300	332	175	177	1	38
150	82.3	12.8	66	248	308	170	175	1	8
230	81.2	13.4	62	263	310	175	177	1	11
350	83.1	14.0	62	274	328†	165	168	1	20
700	86.0	13.8	66	153	335-Neg.	164	169	0	48

* Lead block test with No. 8 detonator = 298 cc.

† Impact test one week later = 32 cm.

TABLE VI

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF ACETIC ANHYDRIDE SUSPENSION OF POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND FUMING SULPHURIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	79.2	13.7	63	278	252	Nil	125	1	23
70	84.0	14.0	67	294	244	Nil	121	0	53
150	82.2	13.8	66	283	335*Neg.	Nil	138	2	45
230	82.6	13.7	64	265	335 Neg.	Nil	124	1	45
350	82.2	13.7	57	283	335 Neg.	Nil	120	1	27
700	81.2	13.5	49	286	335 Neg.	Nil	106	0	53

* Impact test one week later = 36 cm.

Discussion of Results

Previous workers have prepared polyvinyl nitrate by two methods. In the method employed by Frank and Kruger (5), in which a solution of polyvinyl alcohol in concentrated sulphuric acid was added to a cooled nitrating mixture containing excess sulphuric acid, the polyvinyl nitrate was obtained in 80% yield as a yellow-colored product containing only 10% nitrogen, the maximum theoretical value being 15.7%. The preliminary step, in which polyvinyl alcohol was dissolved in concentrated sulphuric acid, was considered necessary to avoid oxidation. In the present investigation it has been shown that powdered polyvinyl alcohol may be added directly to a mixture of fuming nitric acid - fuming sulphuric acid without any appreciable loss by oxidation

simply by carrying out the reaction at -10° to -5° C. The yields were somewhat higher (86 to 89%) and the nitrogen contents of the products (14.2 to 14.9%) were closer to the maximum theoretical value (15.7%).

In the method of Frank and Kruger the polyvinyl nitrate remained in solution in the nitrating acid (since a large excess was employed) but precipitated in the form of yellow-colored plastic granules on heating to 45° to 50° C. In the present method, however, in which a much smaller amount of nitrating acid was employed, the polyvinyl nitrate formed a suspension and was obtained as a colored powder simply by pouring it into ice and water with rapid stirring. It has also been found that polyvinyl nitrate may be prepared by adding an acetic anhydride suspension of polyvinyl alcohol to a mixture of fuming nitric acid and fuming sulphuric acid at -10° to -5° C. Again the product formed a suspension in the nitrating acid and was obtained as a buff-colored powder by pouring it into a mixture of ice and water with rapid stirring. This method likewise gave rise to colored products in 79 to 84% yield with nitrogen contents of 13.5 to 14.0%. This method suffers from the fact that much heat is produced on mixing acetic anhydride and sulphuric acid, thus causing oxidation of the product.

Burrows and Filbert (2, 3), on the other hand, preferred the use of fuming nitric acid alone at 15° to 20° C. in the preparation of polyvinyl nitrate. When powdered polyvinyl alcohol was added to fuming nitric acid at room temperature, it floated on the surface of the nitrating acid, where it tended to ignite and burn with a free flame, forming a carbonaceous residue. This tendency for oxidation to occur was largely avoided by Burrows and Filbert by graining the polyvinyl alcohol. This was accomplished by mixing the latter with sufficient water to render it moist and cohesive, passing it through a 30 mesh screen, and then drying. It was found that this grained material could be more readily immersed beneath the nitrating acid than powdered polyvinyl alcohol, thus reducing the tendency for oxidation to occur. The polyvinyl nitrate remained in solution in the nitrating acid and after stirring at 10° C. for some time the product was obtained in 80.3% yield in the form of a fine cream-colored product containing 13.8% nitrogen by pouring the solution into cold water. In the present investigation it was found that powdered polyvinyl alcohol could be added to fuming nitric acid without preliminary graining (i.e., conversion to particles of 30 mesh size) and without any tendency for the polyvinyl alcohol to burn on the surface of the nitrating acid simply by carrying out the reaction at -10° to -5° C. Polyvinyl nitrates of low degree of polymerization were obtained in the form of fine white powders and those of high degree of polymerization were obtained as a bulky material. The yields (86 to 93%), nitrogen contents (14.6 to 15.0%), and color (white) of the polyvinyl nitrates were better than those reported by Burrows and Filbert.

It has also been shown that polyvinyl alcohol may be nitrated by means of fuming nitric acid and acetic anhydride. In this case, powdered polyvinyl alcohol was added to the nitrating mixture at -10° to -5° C. and the resultant

suspension poured into ice and water, the product thus being obtained in 85 to 92% yield as a white powder containing 13.9 to 14.5% nitrogen.

Finally it was found that, when an acetic anhydride suspension of polyvinyl alcohol was added to a mixture of fuming nitric acid and acetic anhydride, the product was obtained in 81 to 91% yield as a white powder containing 12.8 to 14.9% nitrogen.

These five methods of preparation of polyvinyl nitrates were successfully applied to polyvinyl alcohols obtained from polyvinyl acetates having a degree of polymerization between 30 and 700. The products were generally obtained in the form of a powder, which was purified by grinding in a ball mill in the presence of water. The nitrogen content determined by means of the DuPont nitrometer in no case exceeded 15.0%, the maximum theoretical value being 15.73%. Other esterification reactions of polyvinyl alcohol such as acetylation and benzylation have likewise been found by Staudinger, Frey, and Starck (7) to give rise to incompletely esterified products.

The explosive characteristics of polyvinyl nitrate have not been reported in detail in the literature. Frank and Kruger (5) showed that polyvinyl nitrate may be detonated alone, or mixed with other explosives, either by shock or heat. In its sensitivity to shock and to friction and in its rate of burning it has been found to resemble nitrostarch (4).

In the present investigation it has been shown that polyvinyl nitrate is a very unstable substance, apparently decomposing at room temperature. The Trauzl lead block test indicated a high explosive power. The impact test, however, showed that the sensitivity of polyvinyl nitrate increases markedly when the compound stands at room temperature. The Abel heat test at 70° C. gave low values, indicating instability. The small percentage of carbonyl groups present in polyvinyl alcohol may be responsible in part for this instability. Polyvinyl nitrates cannot be recommended, therefore, as industrial or military explosives even for specialized uses.

Finally, polyvinyl nitrates obtained by all five methods of preparation showed little, if any, relation between explosive properties, nitrogen content, and degree of polymerization.

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SYNTHÈSE DES DÉRIVÉS ORGANOMAGNÉSIENS SANS ÉTHER¹

PAR ROGER BARRÉ ET JACQUES DE REPENTIGNY²

Sommaire

Les conditions d'obtention des dérivés organomagnésiens en l'absence d'éther ont été étudiées et précisées. Nous avons utilisé surtout les hydrocarbures aromatiques et l'éther de pétrole comme solvants, la diméthylaniline comme catalyseur ou support de la réaction. Dans le benzène, le toluène et le xylène, le rendement en iodure d'éthylmagnésium a été 80 à 82%, en bromure d'éthylmagnésium 86%. Les dérivés chlorure de *sec*-butylmagnésium, chlorure d'isomylmagnésium et bromure de phénylmagnésium ont été préparés avec des rendements de 86, 80 et 81% respectivement; on n'a pu préparer le chlorure de *tert*-butylmagnésium. Les dérivés allyl et benzyl donnent de mauvais rendements. Le bromure d'éthylmagnésium et le chlorure de *n*-butylmagnésium ont été obtenus dans l'éther de pétrole avec des rendements de plus de 90%. Les temps de chauffage varient de 5 à 14 h. à 90° C.; la quantité de diméthylaniline varie suivant la nature des dérivés halogénés et les solvants; elle passe de 0.05 molécule-gramme à 1.25 molécule-gramme par molécule-gramme de dérivé halogéné. L'amine joue donc le rôle de catalyseur dans certaines réactions et de support de la réaction dans les autres. La méthode de dosage de ces dérivés Grignard est une modification de la méthode Gilman; pesée du magnésium résiduel et calcul d'après le magnésium consommé, décantation et dosage de l'hydroxyde de magnésium: ce qui donne deux chiffres de rendement. Cette modification permet d'évaluer l'importance des réactions secondaires par la différence de rendement entre les deux chiffres obtenus. Les dérivés Grignard préparés sans éther dans leur condensation avec quelques composés organiques se sont montrés aussi actifs que les dérivés obtenus dans l'éther.

Introduction

Nous avons pensé qu'il serait utile de répéter en les précisant davantage certaines expériences de préparation des dérivés Grignard sans éther. Il y a souvent avantage de pouvoir se servir dans cette réaction de solvants moins volatils que l'éther; ce solvant ne permet pas en effet de faire la condensation à une température élevée alors que souvent l'élévation de la température permet des réactions plus complètes, augmente les rendements et dans certains cas donne même une orientation nouvelle à la réaction. On peut faire la réaction dans l'éther d'abord puis enlever le solvant par distillation et le remplacer par un autre solvant mais il paraît bien préférable d'éliminer cette opération en préparant le dérivé Grignard dans le solvant même qui servira de milieu à la condensation ultérieure.

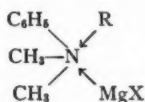
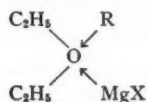
Brühl et Oordt (2) et Malmgren (7) furent les premiers à préparer un dérivé organomagnésien en l'absence d'éther mais ce fut surtout Tschelinzeff (15) qui montra d'une façon certaine la possibilité de préparer ces dérivés Grignard. Il montra que l'azote des amines tertiaires peut remplacer l'oxygène de l'éther dans la formule des RMgX. Il se servit pour cela de la diméthylaniline.

¹ *Manuscrit reçu le 21 février 1949.*

Contribution de l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, P.Q.

² *Présentement à l'emploi de l'Institut de Microbiologie de l'Université de Montréal.*

Toutefois, dans certaines réactions, cet auteur peut diminuer la quantité de diméthylaniline à un point que ce composé ne peut plus jouer le rôle de support de la molécule mais sert plutôt de catalyseur de la réaction.



Spencer *et al.* (12, 13) et Oddo et Del Rosso (9) préparent les RMgX sans aucun solvant autre que l'halogénure. Stadnikov (14) emploie le xylène, Neogi (8) remplace la diméthylaniline par les iodures de trialkylsulfonium et le tétraphénylméthane; Hepworth (5) par les sulfures et les sulfinones organiques.

Gilman (3), Schlenk (10), Shorugin (11) et ses collaborateurs préparent les RMgX sans solvant; Andrianov (1) utilise le tétraéthoxysilicane. Enfin récemment Kuznetzov (6) revient à la diméthylaniline comme catalyseur de la réaction.

Dans notre travail nous avons repris surtout les travaux de Tschelinzeff (15) qui n'a préparé que l'iodure d'éthyle et de phénylmagnésium sans éther.

Dosages

Pour pouvoir traduire nos résultats en chiffres sûrs, nous avons dû nous assurer d'une bonne méthode de dosage des RMgX produits.

Gilman, Wilkinson, Fishel et Meyers (4), après une étude critique des cinq méthodes de titrage des organomagnésiens—titrage à l'iode, analyse gravimétrique, analyse indirecte, analyse volumétrique (Zerewitinoff), titrage par un acide—arrivent à la conclusion que les deux derniers procédés donnent des résultats satisfaisants.

Le titrage par un acide dans la méthode de Gilman consiste à titrer l'hydroxyde de magnésium formé par l'hydrolyse d'une quantité mesurée du dérivé RMgX par un excès connu d'acide sulfurique *N*/1 et à doser l'excès d'acide: c'est la méthode qui semble la plus pratique; dans le cas de dérivés RMgX peu solubles dans l'éther, qui comprennent une bonne partie des dérivés Grignard, Shorugin et ses collaborateurs (11) proposent une modification de la méthode qui consiste à solubiliser ces composés par un mélange à 50% en poids d'éther et de benzène (33 parties de ce mélange pour une partie de magnésium) et à procéder après un repos de 15 à 20 h. comme dans le dosage Gilman. Shorugin reconnaît cependant que souvent cette addition d'éther-benzène déclenche une nouvelle attaque du dérivé halogéné sur le magnésium et que le rendement ainsi peut être augmenté considérablement au cours du dosage lui-même. Nous avons constaté la même chose; comme dans notre cas, nous opérons précisément sans éther, l'addition de ce composé au cours du dosage déclenchait la réaction en faussant nos résultats; même l'addition et la conservation à 0° de la solution éther-benzène-RMgX, nous donnait des chiffres encore trop forts.

Nous avons essayé ensuite la méthode de dosage employée par Tschelinzeff. Celui-ci faisait réagir sur le magnésien obtenu, la benzaldéhyde, et établissait le rendement d'après la quantité de l'alcool secondaire formé. Cette nouvelle méthode de dosage donna des rendements un peu plus sûrs, mais incomplets; en effet l'obtention de l'alcool secondaire n'est pas une réaction quantitative.

Nous avons imaginé alors une technique particulière assez simple mais efficace pour obtenir le pourcentage réel du dérivé RMgX produit.

Après avoir procédé à l'hydrolyse du complexe obtenu dans la synthèse du RMgX, les copeaux de magnésium en excès sont séparés de l'hydroxyde de magnésium par lavage à l'eau dans un bécher; par décantations successives (six à sept), l'hydroxyde de magnésium, étant très fin, reste bien en suspension dans l'eau, alors que les copeaux de magnésium se déposent rapidement au fond du bécher. Cette opération se fait facilement avec un peu de pratique; un examen soigneux de l'hydroxyde décanté et laissé au repos n'a jamais montré des traces de copeaux de magnésium entraîné.

Le résidu de magnésium est recueilli sur un filtre, séché et pesé et un premier rendement est calculé d'après la quantité de magnésium consommé; l'hydroxyde de magnésium est solubilisé dans un excès d'acide sulfurique $N/1$, et titré en retour par l'hydroxyde de sodium $N/1$; nous obtenons ainsi un deuxième chiffre de rendement. On trouve toujours une différence plus ou moins grande entre les rendements calculés par les deux méthodes, premièrement par la quantité d'hydroxyde de magnésium formé après hydrolyse, deuxièmement par le magnésium disparu; elle s'explique par les réactions secondaires qui consomment plus de magnésium qu'indiqué par l'hydrolyse du complexe organomagnésien, produit principal de la réaction; les réactions secondaires donnent surtout du chlorure de magnésium et nous avons vérifié que ce composé n'affecte pas le dosage de l'hydroxyde de magnésium. Le rendement donné par le magnésium consommé est toujours plus élevé que celui donné par l'hydroxyde de magnésium de l'hydrolyse.

Notre méthode de dosage avec ces deux chiffres de rendements nous permet donc d'évaluer avec assez de précision le rendement final de la réaction et aussi chose précieuse, l'importance des réactions secondaires suivant les conditions de la préparation ou de la constitution du dérivé halogéné.

Partie expérimentale

Mode d'opération.—Les essais de synthèse ont été faits dans un appareil standard à joints normalisés, avec agitateur mécanique et dans une atmosphère d'azote séché par un passage dans des flacons laveurs à acide sulfurique; pendant nos expériences, nous avons remplacé les flacons d'acide sulfurique par des tours contenant du "Drierite", éliminant ainsi la possibilité d'entraînement de l'anhydride sulfureux. Nous opérons d'une façon constante avec 5 g. de magnésium (0.20 atome-gramme + 0.14 g. en excès), et une quantité calculée d'halogénure (0.20 mol. gramme). Dix molécules-grammes de solvant et 5 g. de l'halogénure sont mis en réaction dès le début et le reste est ajouté

d'une façon variable suivant les conditions de l'expérience; l'amorce est quelquefois difficile et varie suivant les solvants et le dérivé halogéné; la meilleure est l'iodure d'éthyle qu'on peut ajouter au début en proportion de 1% de l'halogénure employé.

Résultats

Nous avons fait 232 expériences avec divers solvants et dérivés halogénés avant d'arriver aux meilleures conditions de rendement maximum. Nous résumons les résultats dans le tableau suivant: le rendement est basé sur le chiffre donné par le titrage de l'hydroxyde de magnésium obtenu par l'hydrolyse du dérivé RMgX et est une moyenne des meilleurs rendements obtenus. Le chlorure de butyle tertiaire et le bromure d'allyle n'ont pas donné de rendements appréciables.

TABLEAU

RX	Solvant	$\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$, mol. g. (i)	Reflux, h.	T , °C.	Rendement, %
$\text{C}_2\text{H}_5\text{I}$	C_6H_6	0.05	5 - 7	80	82 (ii)
$\text{C}_2\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{CH}_3$	"	"	"	82
$\text{C}_2\text{H}_5\text{Br}$	C_6H_6	0.33	4 - 7	80	96 (ii)
$\text{C}_2\text{H}_5\text{Br}$	Éther de pétrole (80°-100°) (iii)	1	4 - 7	90 - 100	94
$n\text{-C}_4\text{H}_9\text{Cl}$ (iv)	C_6H_6	1.25	11 - 18 (v)	80	90 - 96
$n\text{-C}_4\text{H}_9\text{Cl}$	Éther de pétrole (80°-100°)	"	"	90 - 100	92
$\text{sec-C}_4\text{H}_9\text{Cl}$	C_6H_6	"	14	80	86
$\text{iso-C}_5\text{H}_{11}\text{Cl}$	"	"	"	"	80
$\text{C}_6\text{H}_5\text{Br}$	"	"	"	"	81
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	"	"	"	"	20-30 (vi)

NOTES

- (i) La diéthylaniline, la di-*n*-propylaniline et la di-*n*-butylaniline ont donné des résultats bien inférieurs à ceux fournis par la diméthylaniline.
- (ii) Avec l'iodure d'éthyle et le bromure d'éthyle la diméthylaniline joue le rôle de catalyseur de la réaction mais avec l'éther de pétrole, il faut ajouter assez de ce composé pour qu'il devienne le support de la réaction.
- (iii) L'éther de pétrole doit être très pur. Nous avons utilisé un éther de pétrole fourni par la British Drug House Ltd. L'éther de pétrole du commerce même purifié par distillation et traitement au permanganate de potassium nous a toujours donné des résultats inférieurs. Le magnésium en copeaux doit être aussi très pur sinon les rendements diminuent: le magnésium préparé pour les dérivés Grignard par la compagnie Dow nous a donné complète satisfaction.
- (iv) Le temps d'addition doit être uniforme pour éviter les réactions secondaires que nous constatons par la différence entre les deux rendements obtenus à l'analyse. Voici la meilleure méthode à suivre: ajouter 25% du composé au départ puis 35% après trois heures de reflux et les deux autres 20% après deux heures de reflux respectivement.
- (v) Les meilleurs résultats ont été donnés par 18 h. de reflux; de bons résultats ont été obtenus après 8 et 11 h., mais ils ne sont pas constants.
- (vi) La réaction est entravée par des réactions secondaires: les différences de dosage entre le chiffre donné par l'hydroxyde de magnésium et le magnésium résiduel différent de 35%. Le chlorure de benzyle réagit aussi sur l'amine pour donner un sel quaternaire solide qui nuit à la réaction. Le bromure d'allyle donne aussi avec l'amine un précipité solide qui arrête la réaction.

Condensations

Nous avons fait quelques condensations, afin d'étudier la réactivité des dérivés organomagnésiens préparés ainsi sans éther en présence de diméthylaniline.

Le propionate d'éthyle, en réagissant sur le $n\text{-C}_4\text{H}_9\text{MgCl}$ a donné un rendement de 75% en di- n -butyléthylcarbinol; l'acétone a donné 70% en diméthyl- n -butylcarbinol; la benzaldéhyde a donné un rendement de 66% en butyl- n -phénylcarbinol; et nous avons obtenu 64% en alcool amylique normal à partir du trioxyméthylène. Les deux derniers rendements sont un peu diminués à cause des difficultés rencontrées dans la distillation des produits finaux.

Ces expériences, tout en enlevant tout doute sur la réactivité des dérivés organomagnésiens préparés sans éther, prouvent que ces dérivés sont capables de réagir sur d'autres composés, et de donner des rendements comparables à ceux que l'on obtient dans l'éther.

Dans certaines condensations très vives, il y aurait avantage à utiliser des dérivés organomagnésiens solides, préparés dans un solvant dont le point d'ébullition est plus élevé que celui de l'éther; ces dérivés organomagnésiens étant peu solubles dans certains solvants, la réaction est plus modérée. L'utilisation des RMgX solides peut donc permettre un meilleur contrôle de la marche de certaines condensations trop vives.

Remerciements

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THE REACTION OF NITROGEN ATOMS WITH ETHYLENE¹J. H. GREENBLATT² AND C. A. WINKLER

Abstract

Reaction of nitrogen atoms with ethylene has been found to produce hydrogen cyanide, ethane, and a polymerizable material. The yield of hydrogen cyanide was approximately 70% of the ethylene consumed by nitrogen atoms, while the amount of polymerizable material averaged about 16% by weight of the hydrogen cyanide produced. The yield of ethane increased as the excess of ethylene over nitrogen atoms was increased. The reaction was found to proceed by "clean-up" of nitrogen atoms. An activation energy of 6.9 kcal. was calculated from collision yields, a steric factor of 0.1 being assumed. A mechanism for the reaction has been proposed, involving rupture of the ethylene double bond with formation of hydrogen cyanide and a methyl radical, the methyl radical then reacting further with nitrogen atoms.

Introduction

Although elementary reactions involving atoms and free radicals have been the subject of intensive investigation (18), few kinetic data for the reactions of nitrogen atoms are recorded in the literature. This is doubtless due to the fact that, for many years, it was uncertain whether atoms or metastable molecules were responsible for the enhanced chemical reactivity of nitrogen after it had been subjected to a condensed or electrodeless discharge.

The activity was assigned to metastable molecules when attempts were made to correlate the spectra of the afterglow in "active nitrogen" with its physical and chemical behavior. However, experimental evidence accumulated to indicate that the enhanced chemical activity was due to the presence of nitrogen atoms. The duration of afterglow for as much as six hours under suitable conditions (16), and the direct estimation of nitrogen atom concentrations up to 40% by pressure measurements (24) both favor the conclusion that "active nitrogen" contains atomic nitrogen. Moreover, a second discharge applied externally to the condensed discharge used to activate the nitrogen has been found to excite atomic nitrogen lines (3). The intensity of these lines was found to correlate with the intensity of the afterglow. No atomic nitrogen lines were found when a glowless discharge was used (3), and, in fact, such a discharge has been shown to produce no "active nitrogen" (15). A Stern-Gerlach experiment with active nitrogen, using a silver nitrate target, indicated the presence of nitrogen atoms (12, 13), while more recently (7) it has been shown by pressure measurements that practically complete dissociation of nitrogen into atoms can be obtained in an electrodeless discharge.

The only direct evidence in contradiction to the atomic hypothesis appears to be a failure to observe that decay of the afterglow depended upon triple

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² Holder of a Studentship under the National Research Council of Canada.

collisions (4, 5). However, if the glowing gas is compressed, the intensity of the afterglow varies as $\frac{1}{(\text{volume})^3}$, and also metals such as copper and zinc quench the afterglow (8).

Plausible mechanisms to reconcile the atomic hypothesis with the afterglow excitation have been offered (7).

The reactions of nitrogen atoms with various hydrocarbons have been studied qualitatively by Strutt (20, 21, 22), who found hydrogen cyanide to be the main product, but made no kinetic studies of its formation. The present investigation represents the first of a series by which it is hoped to elucidate the mechanism of the degradation of hydrocarbons by nitrogen atoms.

Experimental

The reaction was studied by the Wood-Bonhoeffer method.

Commercial nitrogen was purified by passing it successively through alkaline sodium hydrosulphite, potassium hydroxide solution, and water. The gas then passed through a calibrated flowmeter and entered the discharge tube through a scratched stopcock.

Ethylene was obtained from the Ohio Chemical Company and from the Polymer Corporation, Sarnia. It was specified to be 99% pure and was used, after a single bulb to bulb fractionation. The rate at which ethylene was admitted from the storage bulb to the reaction vessel was controlled by a scratched stopcock, the amount used in given time being determined from measurements of the initial and final pressures of gas in the storage bulb.

Nitrogen atoms were produced by a high voltage condensed discharge. The electrical circuit consisted of a 4 $\mu\text{f.}$ condenser, which was charged by a 3500 v. half-wave rectifier through a 20,000 to 50,000 ohm resistance, and discharged through the discharge tube across a spark gap. The discharge occurred in pulses, the number of pulses per second depending on the value of the resistance in the circuit and the length of the spark gap. A pulse rate of four to five per second was found to be the most satisfactory.

The discharge tube was a Pyrex tube 70 mm. long and 20 mm. inside diameter, into the ends of which were sealed platinum wires carrying aluminum foil electrodes.

The reaction vessel was a 500 cc. bulb, connecting with the discharge tube through a tube 18 cm. long and 18 mm. diameter. This connecting tube was found necessary to prevent diffusion of ethylene back into the discharge tube. The reddish-violet color accompanying reaction of ethylene with nitrogen atoms was readily detected against the yellow background of the afterglow, and served to indicate the limit of back diffusion of the ethylene.

The products of reaction, together with unreacted ethylene, were withdrawn from the reaction vessel by a three stage mercury diffusion pump backed by an oil pump. The pump passed, on the average, 1.25 liters of gas (S.T.P.) per hour, at a pressure of about 0.5 mm. A liquid air cooled trap

between the reaction vessel and the diffusion pump removed part of the unchanged ethylene together with hydrogen cyanide and other products. The remainder of the gas stream passed through the diffusion pump into a trap containing silica gel and cooled with liquid air. The remainder of the ethylene and large amounts of nitrogen were removed in this trap.

The nitrogen atom concentration was measured with a Wrede gauge, a porous disk being used as a diffusion orifice (6) and the pressure differential across the orifice being measured with McLeod gauges. The atom concentrations were determined in the absence of ethylene, at a point about midway between the reaction vessel and the discharge tube. This position was chosen since at high ethylene concentrations it corresponded to a position almost immediately in front of the reaction zone indicated by the reddish-violet color; under such conditions the reaction vessel was colorless, the absence of nitrogen afterglow indicating the absence of nitrogen atoms beyond the reddish-violet reaction zone (3, 15). With low ethylene concentrations, hence less back diffusion, the atom concentration measured at the position chosen would be somewhat higher than the concentration immediately preceding the reaction zone, owing to some decrease in atom concentration between the point of measurement and the now more distant reaction zone. However, by analogy with the behavior of oxygen atoms (11), the extent of such decrease in atom concentration should be comparatively small.

After each experiment of one-half hour's duration, the total amount of gaseous products in the two traps was determined, followed by analysis of a sample in a Bone and Wheeler gas analysis apparatus. Ethylene was absorbed in mercuric nitrate-nitric acid solution. Combustion analysis of the gas mixture was also made.

Hydrogen cyanide collected in the first trap and was estimated gravimetrically by precipitation with silver nitrate added to the cold trap.

A white material also collected in the upper portion of the inlet tube of the trap, but this material liquefied and became yellow and viscous when attempts were made to distill it to the lower part of the trap. The amount of viscous (polymer) residue was determined by gathering it on to a weighed filter paper.

Results

The data presented in Table I show that, at given nitrogen atom concentration, the amount of hydrogen cyanide produced during a half-hour reaction period is essentially constant (within 10%) over a wide range of ethylene flow rates. The results in Table II show a similar approximate constancy for the amount of ethylene converted to hydrogen cyanide and other products, when the ethylene flow rate is varied as much as fivefold. A small increase in ethylene consumption does occur at higher ethylene flow rates, with corresponding increase in hydrogen cyanide production. This small increase at

TABLE I
PRODUCTION OF HYDROGEN CYANIDE AT VARIOUS NITROGEN ATOM
CONCENTRATIONS AND ETHYLENE FLOW RATES

Temperature: $22 \pm 2^\circ \text{C}$.

Total pressure, mm.	Nitrogen flow rate, moles $\times 10^{-2}$, per 30 min.	Nitrogen atom conc., %	Ethylene flow rate, moles $\times 10^{-2}$, per 30 min.	Hydrogen cyanide produced, moles $\times 10^{-2}$, per 30 min.
0.61	3.0	27	0.50	0.43
0.60	2.7	33	0.56	0.44
0.66	3.0	27	0.95	0.48
0.63	2.9	27	1.13	0.47
0.61	3.0	27	1.19	0.46
0.61	2.8	31	1.30	0.48
0.64	2.9	30	1.42	0.47
		(Av. = 29)		(Av. = 0.46)
0.54	2.8	23	0.75	0.40
0.54	2.8	21	0.76	0.37
0.55	2.8	18	0.92	0.35
0.66	3.0	22	0.95	0.35
0.53	2.9	22	1.05	0.39
0.57	2.9	23	1.18	0.41
		(Av. = 22)		(Av. = 0.38)
0.59	2.6	17	0.71	0.31
0.58	2.5	16	0.94	0.27
0.62	2.6	16	1.00	0.31
0.58	2.6	14	1.21	0.29
		(Av. = 16)		(Av. = 0.30)

TABLE II
CONSUMPTION OF ETHYLENE AND PRODUCTION OF HYDROGEN CYANIDE, SATURATED PRODUCTS,
AND POLYMERIZABLE MATERIAL AT VARIOUS ETHYLENE FLOW RATES
WITH GIVEN NITROGEN ATOM CONCENTRATION

Temperature = $22 \pm 2^\circ \text{C}$.

Total pressure, mm.	Nitrogen flow rate, moles $\times 10^{-2}$, per 30 min.	Nitrogen atom conc., %	Ethylene flow rate, moles $\times 10^{-2}$, per 30 min.	Ethylene recovered, moles $\times 10^{-2}$, per 30 min.	Ethylene reacted, moles $\times 10^{-2}$, per 30 min.	Ethylene converted to saturated products, moles $\times 10^{-2}$, per 30 min.	Ethylene converted to hydrogen cyanide, moles $\times 10^{-2}$, per 30 min.	Hydrogen cyanide produced, moles $\times 10^{-2}$, per 30 min.*	Hydrogen cyanide produced, gm. per 30 min.	Polymerizable material produced, gm. per 30 min.
0.64	3.0	29	0.29	0.00	0.29	0.00	0.29	0.43	0.116	0.012
0.60	2.8	31	0.30	0.00	0.30	0.00	0.30	0.43		
0.61	3.0	27	0.50	0.16	0.34	0.063	0.28	0.43		
0.60	2.7	33	0.56	0.23	0.33	0.049	0.28	0.44		
0.66	3.0	27	0.95	0.49	0.46	0.102	0.36	0.48	0.130	0.020
0.63	2.9	27	1.13	0.69	0.44	0.072	0.36	0.47	0.127	0.016
0.61	3.0	27	1.19	0.71	0.48	0.094	0.38	0.46	0.124	0.020
0.60	2.7	28	1.19	0.76	0.43	0.098	0.33			
0.61	2.8	31	1.30	0.74	0.56	0.120	0.35	0.48	0.130	0.026
0.63	2.9	30	1.42	0.89	0.53	0.165	0.37	0.47		

* The values in this column are not twice those in the preceding column, owing to the presence of polymerizable product.

higher flow rates is probably due to displacement of the reaction zone nearer to the discharge tube, where the atom concentration is slightly higher. Considered as a whole, the data indicate that reaction proceeds by a "clean-up" of nitrogen atoms.

A limiting value of the ethylene flow rate was found, below which the amount of hydrogen cyanide produced varied linearly with ethylene flow rate at given atom concentration. The data illustrating this behavior are plotted in Fig. 1. In the range represented, nitrogen atoms were in excess,

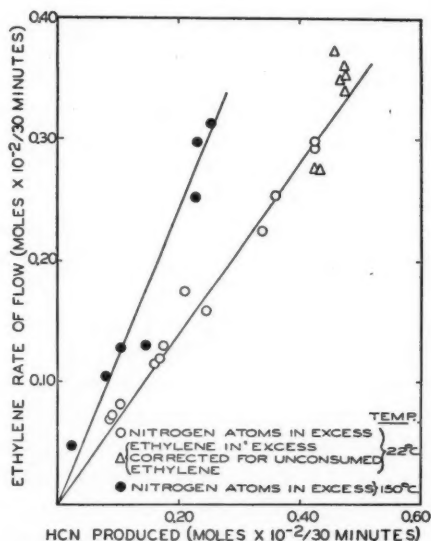


FIG. 1. Production of hydrogen cyanide at various ethylene flow rates at 22° C. and 150° C.

and all the ethylene was consumed. The plot therefore represents the maximum amount of hydrogen cyanide that can be obtained in the presence of excess nitrogen atoms. On the same figure are shown some values for the amount of ethylene converted to hydrogen cyanide and other products in experiments where ethylene was in excess (Table II). These points also lie satisfactorily close to the line, since in effect the values of ethylene flow rate have been corrected for unconsumed ethylene and ethylene converted to saturated products, i.e., corrected back to the critical limit of ethylene flow rate.

When the data of Fig. 1 are brought together with data from Tables I and II and from eight experiments for which details have not been given, the summary represented in Fig. 2 is obtained. In the additional eight experiments only ethylene input and hydrogen cyanide production were measured, but the

conditions under which the experiments were made were similar to those where the nitrogen atom concentrations averaged 22% and 16%, and the amounts of hydrogen cyanide produced per half-hour period agree with the values shown in Table I for these atom concentrations.

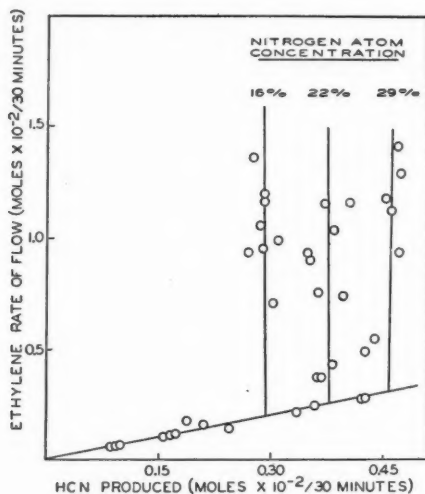


FIG. 2. Production of hydrogen cyanide at various ethylene flow rates and nitrogen atom concentrations.

In Fig. 2, the vertical lines show the constancy of hydrogen cyanide production, above a critical limit of ethylene flow rate, for three nitrogen atom concentrations. Such a vertical line could be realized experimentally at any atom concentration. A point on the sloping line, corresponding to any given atom concentration, defines the critical flow rate of ethylene below which consumption of ethylene is complete at that nitrogen atom concentration. The whole behavior reflected in Fig. 2 conforms to a "clean-up" reaction.

The saturated products were inferred from explosion analysis to consist almost entirely of ethane. If methane and hydrogen were products of the reaction they were either formed in amounts that were too small to be detected by this method of analysis, or they were not retained in the silica gel trap in the presence of large amounts of nitrogen. The amount of ethylene converted to saturated products increases from undetectable amounts at low ethylene flow rates to considerable amounts at high ethylene flow rates. However, the amount of ethylene converted to hydrogen cyanide and products other than saturated hydrocarbons remains relatively constant, as does also the amount of hydrogen cyanide obtained. It would seem, therefore, that the production of saturated products does not occur in the same reaction as that in which hydrogen cyanide is produced.

Estimation of the polymerizable material, although only approximate, leaves little doubt that it is produced in comparatively small amount, and that hydrogen cyanide is to be considered as the main product of the reaction.

The reaction was also studied at 150° C. The results are shown in Fig. 1 together with those obtained at the lower temperature. It will be noted that, at the higher temperature, a smaller amount of hydrogen cyanide was obtained from a given amount of ethylene in the presence of excess nitrogen atoms.

Calculations of collision yields were made for only a few of the experiments. With "clean-up" occurring, the amount of ethylene consumed by reaction with nitrogen atoms is constant above the critical value of ethylene flow rate. Thus, while percentage conversions of ethylene based on total ethylene flow are variable, the percentage conversions based on ethylene consumed by nitrogen atoms remain constant. Since, at high ethylene concentrations, only a portion of the reaction vessel is occupied by the reacting gases, the calculations were made for experiments at the critical ethylene flow rate, when the reacting gases filled the reaction vessel and a more accurate estimate of reaction time was possible. Under these conditions, all the ethylene reacts, but only about 75% of it is converted to hydrogen cyanide. It is, then, a question whether formation of the remaining products depends upon the same rate controlling step as formation of hydrogen cyanide, i.e., a step involving reaction with a nitrogen atom. If it does, then the conversion could be taken as 100%, only 75% of the products emerging as hydrogen cyanide. If, however, hydrogen cyanide is formed by a different initiating reaction, the percentage conversion for the main reaction would be 75%. Calculations were made using both 75% and 100% conversion values. These calculations should give an upper and lower limit respectively for the activation energy.

The number of collisions per second of one ethylene molecule with nitrogen atoms is given by

$$Z_{C_2H_4-N} = 2\sqrt{2\pi} \cdot N_N \left(\frac{d_N + d_{C_2H_4}}{2} \right)^2 \left(\frac{M_N + M_{C_2H_4}}{M_N \cdot M_{C_2H_4}} \cdot RT \right)^{\frac{1}{2}}$$

where M_N and $M_{C_2H_4}$ are the respective molecular weights of the nitrogen atom and ethylene molecule, d_N and $d_{C_2H_4}$ their molecular diameters, and N_N is the number of nitrogen atoms per cubic centimeter. The value of d_N was taken as 2.98×10^{-8} cm.; from Rayleigh's assumed value for the coefficient of self-diffusion of nitrogen atoms (17). A value of 3.5×10^{-8} was used for $d_{C_2H_4}$ (14). The activation energies were calculated from the relation

$$\text{Collision yield} = A e^{-E/RT}$$

a value of 0.1 being assumed for the steric factor, A .

The data used for the calculations and the results obtained are given in Table III.

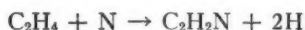
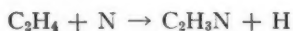
Discussion

Both the upper limit of 7.0 kcal. and lower limit of 6.8 kcal. calculated for the activation energy may be regarded as too high, since the atom concentration used in the calculations is that measured near the entrance to the reaction vessel during experiments in which no ethylene was flowing, and is not the average concentration during reaction. In the experiments for which the calculations were made the ethylene flow rate was just at the critical limit. Hence consumption of nitrogen atoms was practically complete, and the steady state concentration of nitrogen atoms probably much lower than the value used in the calculations.

The value of 0.1 taken for the steric factor is also suspect. While this is the value that it has been customary to assume for calculating activation energies from collision yields in analogous hydrogen atom reactions, there are reasons to believe that a smaller steric factor should be used (18, 20, 21, 22). The adoption of a smaller steric factor would result in a lower value of the calculated activation energy.

An attempt to formulate a mechanism for the reaction between nitrogen atoms and ethylene is handicapped by lack of experimental data on the strength of carbon-nitrogen bonds, and by lack of kinetic data on nitrogen atom reactions generally. It is possible, however, to suggest a mechanism that can account reasonably well for the experimentally observed results.

The most recent estimates (18) for bond strengths give values ranging from 90 to 100 kcal. for the C-H bond, about 80 kcal. for the C-C bond and about 60 kcal. (9) for the C-N bond. Hence, all reactions involving replacement of one or more hydrogen atoms by nitrogen would be endothermic. Examples of such possible reactions are:



Such reactions are endothermic by as much as 30 kcal. or more, hence do not appear probable as the initial step in a "clean-up" reaction.

A second possibility is the addition of a nitrogen atom to form an activated complex, perhaps of free radical type:



This reaction would be exothermic. It could be followed by a rearrangement to split off hydrogen cyanide, or by a second collision with a nitrogen atom to form two molecules of hydrogen cyanide and two hydrogen atoms. The probability of this second collision is smaller than the probability of (1), owing to depletion of nitrogen atoms by (1). Moreover, if the necessary collision did occur the reaction would be about 40 kcal. endothermic, with a

correspondingly small probability of occurrence. Thus, rearrangement of the activated complex in (1) with formation of hydrogen cyanide appears more probable. The initial step might therefore be represented:



This reaction actually involves the simultaneous rupture of a double bond and migration of a hydrogen atom, and is about 25 kcal. exothermic. One-step mechanisms of this type, in which scission and re-formation of bonds occur with simultaneous migration of hydrogen atoms, have been proposed by Bawn and Milsted (2) and by Bawn and Dunning (1) to account for ethylene formation in reactions of the type

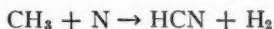


Ethylene is obtained even when hydrogen is used as the carrier gas. These authors take this as evidence for the absence of a CH_3CH radical, on the grounds that if it were present ethane should be formed.

Following upon (2), the following reactions might be assumed to occur:



Reaction (4) is suggested in preference to the reaction



since assumption of the latter makes it difficult to account for the observed increase in amount of saturated products with increased excess ethylene. Reaction (4) should have a high probability since consumption of ethylene is complete when nitrogen atoms are in excess. If (5) occurred, under these conditions of excess nitrogen atoms, the higher hydrocarbons formed would also be broken down to hydrogen cyanide by reaction with nitrogen atoms. With excess ethylene present Reaction (5) might be expected, leading to the formation of higher hydrocarbons, which were not found however, among the products. The nonoccurrence of (5) can be explained by the observation that under these conditions the reaction zone occupied only a small portion of the reaction vessel and a portion of the connecting tube. This means that at high ethylene concentrations the ethylene diffused out of the reaction vessel against the gas stream, towards the discharge tube, the reddish violet reaction zone marking the extent of mutual penetration before complete consumption of one or other component. Thus, in this zone there exists no large excess of ethylene, and Reaction (5) would have small probability.

The ethane formed when ethylene was in excess was presumably formed by hydrogenation of ethylene, as in Reactions (6) and (7). The hydrogenation of ethylene has recently been reviewed by Steacie (18), the general conclusion being that the nature of the products obtained depends upon the hydrogen-ethylene ratio. At moderate hydrogen concentrations, ethane is formed exclusively. Reaction (6) occurs readily, and has been assigned an activation energy of about 5 kcal. (18).

The amount of polymerizable material formed in a given time by the reaction of nitrogen atoms with ethylene was probably constant, since the yield of hydrogen cyanide (about 70% of the ethylene consumed by nitrogen atoms) was reasonably constant. Difficulty in handling the small amount of material obtained during an experiment made it impossible to obtain a sample that could be considered sufficiently pure to justify an analysis of it. Consequently, nothing is known about the composition or probable mechanism of formation of the polymerizable material.

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APPLICATION OF DIFFUSION FLAME TECHNIQUE TO THE REACTION BETWEEN NITROGEN ATOMS AND ETHYLENE¹

J. H. GREENBLATT² AND C. A. WINKLER

Abstract

Rate constants for the reaction between nitrogen atoms and ethylene have been obtained by diffusion flame technique over the temperature range 273° to 373° C. An activation energy of about 3 kcal. has been obtained from the temperature coefficient of these rate constants, and using this value a steric factor of 10^{-2} has been calculated.

Introduction

The diffusion flame method of measuring reaction rates was developed originally by Polanyi and coworkers for studying the reactions between sodium atoms and various organic halides (2, 3, 4, 5). The rate constant was inferred from measurements of the distance one component diffused into another before being consumed by reaction. Obviously, successful application of the method requires demarcation of the reaction zone from the surrounding gas. In the method as originally developed, a carrier gas was passed through liquid sodium at 250° C. and then through a jet coaxially mounted in a larger tube, where the sodium vapor diffused into, and reacted with, the organic halide. The extent of diffusion was determined by exciting fluorescence in the sodium vapor with a resonance lamp.

It is evident that the extent of mutual penetration of the vapors should be greater, the slower the reaction rate. In formulating this relation, three assumptions must be made:

(i) The flow of inert gas should be fast enough to prevent diffusion of the organic halide back into the jet. The concentration of the emergent sodium vapor is then not decreased by reaction within the jet.

(ii) The rate of flow of carrier gas in the tube surrounding the jet should be slow enough that distribution of the reactants occurs by diffusion only, the influence of mass flow being negligible. If the distribution of the halogen compound is not influenced by the flow then, if its consumption by sodium vapor is ignored, it should have the same partial pressure, p_{Hal} , throughout the reaction space.

(iii) The flame diameter should be smaller than that of the reaction vessel, to eliminate influence of the wall.

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² Holder of a Studentship under the National Research Council of Canada.

By applying steady state calculations for the condition that the partial pressure of the halogen compound is constant at p_{Hal} throughout the reaction space and drops to zero at the jet, Hartel and Polanyi (3) obtained

$$k = \frac{\left(\ln \frac{p_{\text{jet}}}{p_0}\right)^2}{\frac{d^2}{4}} \cdot \frac{D}{p_{\text{Hal}}},$$

where p_{jet} = partial pressure of sodium vapor at the jet,

p_0 = partial pressure of sodium vapor at the edge of the flame,

p_{Hal} = partial pressure of the halide,

d = diameter of the flame,

D = diffusion coefficient of the sodium vapor under the conditions of the experiment.

As reported previously (1), the reaction between nitrogen atoms and ethylene is accompanied by a reddish violet color that may be differentiated reasonably well from the yellow afterglow associated with the presence of nitrogen atoms. This suggested that diffusion flame technique might be applied to the reaction between nitrogen atoms and ethylene. In this way, by evaluating the activation energy, it was hoped to obtain a direct estimate of the steric factor for the reaction.

Experimental

Nitrogen atoms were produced by the Wood-Bonhoeffer method, as described previously (1). The pumping system and methods of gas purification, flow control, and measurement of atom concentration are all outlined in the previous paper.

It was necessary to make one modification to the apparatus used for the earlier study. The reaction vessel for the present study consisted of a tube 55 mm. in diameter and about 30 cm. long. Into one end was sealed coaxially a jet of 2.5 mm. diameter through which the ethylene was introduced into the reaction vessel. The yellow mixture of nitrogen atoms and nitrogen molecules was pumped from the discharge tube, through a wide connecting tube, to the reaction vessel, which was connected directly to the pumping system by large diameter tubing, without any trapping system in the line. It was surrounded with a jacket fitted with a heating coil and a large window through which observations of the flame size could be made.

By proper regulation of the rates of flow of both gases, reasonably spherical flames were produced. The diameters of the flames were measured directly with a centimeter scale. Although it is hoped to improve upon this method in future studies of similar systems, it was found that, with some practice and in a darkened room, the dimensions of the reaction zone could be approximately determined by this simple procedure. The reddish-violet color of the reaction zone has been identified with the cyanogen spectrum (6, 7, 8) and appears to

be observed generally in the attack of hydrocarbons by nitrogen atoms, the end product being hydrogen cyanide. The cyanogen spectrum was also observed when cyanogen was introduced into a vessel containing nitrogen atoms, but was not obtained when hydrogen cyanide was used in place of cyanogen. Hence, the reddish violet color can be associated with reactions involving the formation of a carbon-nitrogen bond. The flame boundary may then be taken to represent the limit of diffusion of a hydrocarbon or a free radical derived from the hydrocarbon into the nitrogen atom mixture. A rate constant calculated from the flame diameter should therefore give the rate of the over-all reaction.

The various partial pressures required for calculating a rate constant were obtained from the experimentally evaluated total pressures and mole fractions. For ethylene, the pressure so obtained would be the pressure of ethylene in the system with no reaction occurring, and it was assumed that this was the emergent pressure at the jet. The limiting pressure of ethylene was obtained by decreasing the rate of ethylene flow until the small reaction zone was practically indistinguishable from the yellow background of the afterglow. The partial pressure of ethylene (9×10^{-4} mm.) at this very low flow rate was taken as that at the edge of the reaction zone where the reddish-violet and yellow colors merged.

The diffusion coefficient used in the calculations was that for self-diffusion of ethylene. This seems reasonable, since nitrogen and ethylene have the same molecular weight and almost identical collision diameters, and the concentration of nitrogen atoms is small compared with that of nitrogen molecules. Collision diameters for ethylene, taken from Landolt-Börnstein (Roth-Scheel) Tabellen, average 3.5×10^{-8} cm. while values for nitrogen range from 3.1 to 3.8×10^{-8} cm.

Results and Discussion

The experimental conditions and results are given in Table I. There is little doubt that the absolute values of the rate constants are considerably in error, but they are almost certainly not in error by a factor exceeding three or four. The relative values at different temperatures are of greater interest, since they indicate that the increase in rate constant over the temperature range studied is of the same order of magnitude as variations in the value of the rate constant at a given temperature. It can safely be stated that the rate constant does not increase by more than a factor of two or three over the range studied. This fact indicates an activation energy lower than the value of 6.9 kcal. calculated from collision yields for the reaction (1).

The values for the rate constants at the higher temperatures are more likely to be in error than those at lower temperatures, owing to the difficulty of obtaining a reasonably large spherical reaction zone with the smaller atom concentrations at the higher temperatures. Hence, only the range from 273° to 325° K. will be considered for obtaining a value of the activation energy.

TABLE I
EXPERIMENTAL CONDITIONS AND RATE CONSTANTS FOR REACTION OF NITROGEN ATOMS WITH ETHYLENE IN DIFFUSION FLAME

Nitrogen flow rate, moles/sec. $\times 10^6$	Nitrogen atom conc., %	Nitrogen atom flow rate, moles/sec. $\times 10^6$	Ethylene flow rate, moles/sec. $\times 10^6$	Total flow rate— corrected for nitrogen atoms, moles/sec. $\times 10^6$	Total pressure, mm.	$p_{C_2H_4}$, mm.	d , cm.	D_c (calc.)	k , sec. $^{-1}$ mm. $^{-1}$	Average k , sec. $^{-1}$ mm. $^{-1}$
Temperature = 273° K.										
4.04	21	0.94	0.098	4.60	0.74	0.152	4.3	88	0.95×10^8	1.4×10^8
4.04	21	0.94	0.129	4.64	0.75	0.153	3.6	87	1.7×10^8	
4.04	21	0.94	0.096	4.61	0.74	0.151	3.7	88	1.4×10^8	
Temperature = 295° K.										
4.14	20	0.92	0.111	4.61	0.76	0.151	3.5	96	1.9×10^8	1.3×10^8
4.16	20	0.92	0.118	4.74	0.71	0.139	5.0	103	1.1×10^8	
4.16	20	0.92	0.113	4.74	0.78	0.151	4.5	94	1.1×10^8	
4.15	20	0.92	0.137	4.75	0.71	0.137	5.1	104	1.2×10^8	
Temperature = 298° K.										
4.04	21	0.94	0.098	4.61	0.85	0.173	4.8	87	0.8×10^8	1.1×10^8
3.99	21	0.93	0.067	4.52	0.81	0.167	3.4	90	1.3×10^8	
Temperature = 325° K.										
4.10	14.5	0.65	0.064	4.45	0.74	0.107	5.0	117	1.1×10^8	1.3×10^8
4.05	14.5	0.64	0.072	4.44	0.74	0.107	5.7	116	0.9×10^8	
4.05	14.5	0.64	0.054	4.42	0.74	0.106	3.5	117	1.9×10^8	
Temperature = 328° K.										
4.31	14	0.65	0.080	4.71	0.76	0.105	3.4	112	2.6×10^8	3.1×10^8
4.36	14	0.65	0.064	4.75	0.80	0.110	2.6	107	3.6×10^8	
Temperature = 348° K.										
3.89	10	0.41	0.044	4.04	0.90	0.091	5.2	105	1.0×10^8	1.0×10^8
Temperature = 377° K.										
3.88	7	0.28	0.029	3.95	0.90	0.064	4.2	117	1.6×10^8	1.6×10^8

For the rate constant to double over this range of temperature, the activation energy must be about 3 kcal. An activation energy of 3 kcal. would give a ratio of $\frac{k_{328}}{k_{273}} = 2.5$, while an activation energy of 2.5 kcal. would give $\frac{k_{328}}{k_{273}} = 2.1$. Thus, an activation energy of not more than 3 kcal. is indicated.

Values of the steric factor were calculated from the rate constants in Table I, a value of 3 kcal. being assumed for the activation energy. The steric factors were calculated by expressing the rate constant as

$$k = pZ \cdot e^{-E/RT},$$

where p is the steric factor and Z the collision number per second, given by

$$Z = d_{av}^2 \left(8\pi RT \frac{M_N + M_{C_2H_4}}{M_N \cdot M_{C_2H_4}} \right)^{1/2}$$

for one molecule of each reactant per cubic centimeter. The mean collision diameter, d , was obtained from the values 2.98×10^{-8} cm. and 3.5×10^{-8} cm. for nitrogen atoms and ethylene respectively. The calculated steric factors are given in Table II. The tabulated values indicate that a steric factor slightly higher than 10^{-2} is associated with the reaction followed by the dilute flame technique.

TABLE II
VALUES OF k IN SEC.^{-1} ($\text{MOLECULES/CC.})^{-1}$ AND CORRESPONDING STERIC FACTORS AT VARIOUS TEMPERATURES

T , °K.	$p, \times 10^{-2}$	k , $\text{sec.}^{-1}(\text{molecules/cc.})^{-1}$
273	2.7	2.68×10^{-14}
273	3.0	4.96×10^{-14}
273	3.9	3.86×10^{-14}
295	3.4	5.72×10^{-14}
295	1.9	3.22×10^{-14}
295	2.1	3.47×10^{-14}
295	2.1	3.50×10^{-14}
298	1.4	2.41×10^{-14}
298	2.1	3.81×10^{-14}
325	1.3	3.55×10^{-14}
325	2.3	6.36×10^{-14}
325	1.1	2.98×10^{-14}
328	3.0	8.80×10^{-14}
328	4.0	1.17×10^{-13}

If, in the previous study (1), a steric factor of 10^{-2} , instead of 10^{-1} , had been used, to calculate the activation energy from collision yield data, a value of 5.5 kcal. would have been obtained. There remains, therefore, a discrepancy of 2.5 kcal. between the value of 3 kcal. indicated by the present study and the recalculated value for the previous investigation. This corresponds to a difference in collision yields of approximately 10^2 for the two investigations.

There is no reason to suppose that this discrepancy has any significance other than to indicate the limitations of the data obtained by the two methods of studying the reaction. The rather drastic assumptions made in calculating the rate constants from the diffusion flame data should affect the absolute values of the rate constants much more than the relative values for different temperatures. Since the absolute values were used to calculate the steric factor of approximately 10^{-2} , it is possible that this value is considerably in error. Also, the activation energies obtained from collision yield data are doubtless too high, since the values for nitrogen atom concentrations used in the calculations were those measured in the absence of reaction. It might be argued that a similar consideration should apply to the diffusion flame method, even though, in this case, the reaction zone is surrounded by an excess of nitrogen atoms at essentially constant partial pressure. However, in the diffusion flame system, nitrogen atoms can be at least partially replenished in the flame by diffusion all around the periphery of the reaction zone, a condition that does not obtain in the first type of system used. The diffusion flame method should therefore be less subject to error from discrepancies between the measured atom concentrations and those actually present during reaction.

Everything considered, it seems reasonable to assign an activation energy of 3 to 5 kcal., with a steric factor not exceeding 10^{-2} , to the reaction of nitrogen atoms with ethylene.

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